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INCREASE IN TEMPERATURE OF CELLULOSE ON ABSORPTION OF ATMOSPHERIC MOISTURE.

By CLAYTON BEADLE.

I HAVE already pointed out (*Nature*, xlix., 457) that "cellulose, when rendered anhydrous by placing it in a water-bath or desiccator, is found to rise considerably in temperature when exposed to a damp atmosphere. This may, however, be caused by the liberation of heat, due to the condensation of moisture from the gaseous state. If so, no rise in temperature would be noticed in plunging anhydrous cellulose into water." . . . "I have found that dry cellulose placed in a damp atmosphere remains at a higher temperature than its surroundings so long as it is taking up moisture, which appears to be greater when the rate of absorption is greatest. By the time it has recovered its normal condition of moisture, it has sunk to the temperature of its surroundings."

Since the above observations were made I have completed a number of experiments in this direction. These experiments, in my mind, clearly indicate that some sort of a union takes place between the cellulose and the moisture, that it assimilates, and that this union is attended by the liberation of heat.

In the following experiments the amount of heat liberated must be much greater than that indicated by the rise of temperature of the thermometer imbedded in the cellulose, since the specific heat of the thermometer is many times greater than that of the cellulose. They serve to show, however, the variations of temperature as the moisture is absorbed. Those marked with an asterisk show where air was blown against the cellulose. It will be noticed that wherever this is done the assimilation of moisture has been more rapid, and also the difference in temperature between the cellulose and surrounding air has been increased. Even when the difference has remained stationary for a short time, a blast of air will cause a further increase. I find, moreover, that the rise of temperature is greatest when the surrounding air is charged with moisture. It appears probable that the amount of moisture assimilated bears a direct relation to the heat liberated, but no conclusion can be arrived at until actual measurements of the heat liberated have been made and compared directly with the rate of absorption.

Two Grms. of Cotton-Wool Previously Dried in Air-Bath at 220° F.
(For increase in weight during absorption).

1.	2.	3.	4.	5.
0	92·85			
1	93·10	0·25	0·25	0·25
2	93·3	0·45	0·20	0·20
*3	93·7	0·85	0·40	0·40
4	93·9	1·05	0·20	0·20
5	94·2	1·35	0·30	0·30
6	94·55	1·70	0·35	0·35
7	94·75	1·90	0·20	0·20
8	95·00	2·15	0·25	0·20
10	95·35	2·50	0·35	0·18
12	95·65	2·80	0·30	0·15
17	96·20	3·35	0·55	0·11
22	96·60	3·75	0·40	0·08
*27	97·55	4·70	0·95	0·19
*32	98·15	5·30	0·60	0·12
*37	98·55	5·70	0·40	0·08
*42	98·90	6·05	0·35	0·07
47	99·05	6·20	0·15	0·03
52	99·15	6·30	0·10	0·02
62	99·15	6·30	0·00	0·00

1. Time in minutes of exposure.
2. Weight of cotton on assumption that air-dry weight equals 100.
3. Gain per cent on air-dry weight.
4. Gain since last weighing.
5. Gain per minute.

Two Grms. of Cotton-Wool Dried in Desiccator for Twenty-four Hours.
(For increase of temperature during absorption).

6.	7.	8.	9.		10.
0	57·0°	57·0°	0·0		
1	57·0°	57·5	0·5	+	0·5
2	57·0°	58·0	1·0	+	0·5
3	57·0°	59·3	2·3	+	1·3
4	57·0°	60·5	3·5	+	1·2
5	57·0°	61·0	4·0	+	0·5
8	56·8°	60·5	3·7	−	0·1
*10	57·0°	60·0	3·0	−	0·35
*11	57·0°	59·7	2·7	−	0·3
18	57·3°	59·0	1·7	−	0·15
29	57·8	58·5	0·7	−	0·09
46	58·0	58·0	0·0	−	0·04

Two Grms. of Cotton-Wool Dried in Air-Bath at 220° F.
(For increase of temperature during absorption).

.	7.	8.	9.		10.
0	56·5	56·5	0·0		0·0
1	56·8	57·2	0·4	+	0·4
2	56·5	58·0	1·5	+	1·1
5	56·3	59·2	2·9	+	0·5
6	56·3	59·7	3·4	+	0·5
7	56·3	60·0	3·7	+	0·3
8	56·3	60·2	3·9	+	0·2
9	56·3	60·4	3·9		0·0
*10	56·3	60·7	4·4	+	0·5
*12	56·2	60·9	4·7	+	0·15
13	56·2	61·0	4·8	+	0·1
15	56·6	61·4	4·8		
*16	56·6	61·6	5·0	+	0·2
20	56·2	61·2	5·0		
26	56·0	60·8	4·8	−	0·05
31	56·0	60·0	4·0	−	0·16
39	56·2	59·3	3·1	−	0·11

6. Time of exposure in minutes.
7. Temperature of air (degrees F.).
8. Temperature of cotton (degrees F.).
9. Difference between 7 and 8.
10. Rate of increase (+) or decrease (−) of difference during interval, expressed in degrees per minute.

ACTION OF METALLIC MAGNESIUM UPON MANGANOUS SALTS.

By JOS. G. HIBBS and EDGAR F. SMITH.

The statements relating to the action of metallic magnesium upon solutions of manganous salts are contradictory; thus Manck ("Ueber d. Verh. d. Magnesium und Aluminium gegen Salzlösungen," Goettingen, 1862) states that metallic manganese is readily precipitated by magnesium from neutral solutions of manganous nitrate or chloride. Phipson (*Jahresb.*, 1864, 192) corroborates this, and remarks that the manganese separates as a regulus. The observations of Roussin (*Jahresb.*, 1866, 170), Comaille (*Comptes Rendus*, lxiii., 556; *Jahresb.*, 1866, 171), and Kern (Chemical News, xxxiii., 236), on the other hand, seem to demonstrate that metallic manganese is not thrown out of manganous salts by metallic magnesium.

We have tried the action of the last metal on manganous salt solutions, both in the presence of alcohol and ether. In using these liquids, our aim was to reduce the liability of oxidation of manganese, if any should appear, to a minimum.

Experiment 1.—In this trial magnesium acted upon aqueous manganous chloride in the presence of alcohol for a period of two hours. At the expiration of this time the liquid was distilled off, and the material remaining was then carefully analysed. 0·2582 grm. substance was used for this purpose. It showed the presence of 0·0284 grm. of chlorine, 0·1392 grm. of magnesium, and 0·0539 grm. of manganese, or a total of 0·2215 grm.

Experiment 2.—In this both ether and alcohol were added to the solution upon which the magnesium acted. After removal of the liquids the residue was dried in an atmosphere of nitrogen. 0·6530 grm. of it showed the presence of 0·0993 grm. of chlorine, 0·3059 grm. of magnesium, and 0·1865 grm. of manganese, or a total of 0·5917 grm. The action of the magnesium in this instance was only continued through one and a half hours.

Experiment 3.—The conditions here were practically the same as those in Experiment 2. The substance was dried, as there, in an atmosphere of nitrogen. Upon analysing 0·7120 grm. of the dry residue, it revealed the presence of 0·2302 grm. of chlorine, 0·2339 grm. of magnesium, and 0·1779 grm. of manganese.

In these three trials, as in others which were made, the sum total of the constituents of the reaction product, obtained by analysis, is less than the quantity of material taken for analysis, indicating that, in all probability, it is not metallic manganese which is precipitated by magnesium, but rather a hydrated oxide, as was suggested by Kern, who used a saturated solution of manganous chloride, and allowed metallic magnesium to act upon it for a period of six to eight hours, with this result—

$$3MnCl_2+3Mg+3H_2O=3MnO+3MgCl_2+3H_2,$$

and in the presence of water the manganous oxide passes into the protosesquioxide.

Metallic manganese thrown out by the electric current oxidises rapidly on momentary contact with the air, and even if it should come down as metal, through the action of magnesium, it is scarcely probable that, in the finely divided state in which it would be, it could long resist the action of the surrounding water.—*Journal of the American Chemical Society*, xvi., No. 12.

A REVOLUTION IN VOLTAIC ELECTRICITY.

The Boron Carbon Battery.

By H. N. WARREN, Research Analyst.

The numerous voltaic cells that are constantly described upon the pages of scientific literature, and after all which are so modest as regards their voltage, naturally suggest an apology to offer yet another. The above title is not, however, too ambitious, when I may mention that after a lengthy and troublesome research I have had the satisfaction of arranging a battery capable of producing 3 volts and giving a constant current from 2 to 2·5 for almost unlimited duration. Such a battery may be in some measure approached by either Bunsen or Grove's cell; but in mine there is a complete absence of fuming acid, and it costs less than one penny for ten hours' action. The cells themselves are constructed upon the flat system, with sliding carbon plates enclosed in teak-wood boxes, the carbons being chemically prepared by special treatment, whereby gaseous compounds of boron are so decomposed as to allow of the boron becoming absorbed into the pores of the carbon, which are afterwards soaked in solution of oxalate of platinum, and heated to redness in an atmosphere of hydrogen. A flat porous cell encloses the zinc element, while the outer cell contains a specially prepared manganic salt in admixture with other substances.

The cells are for several reasons arranged in a series of three, and thus readily constructed for voltage or quantity, and complete up to 50 ampères, the cost at the commencement being no greater than batteries that afford only half the power.

As illustrative of the power of these particular cells, twelve small ones were arranged in a series, the arc produced between the carbon points being more than the naked eye could bear. Over two feet of platinum wire was raised to incandescence, whilst the heat from the arc produced readily fused titanium, chromium, and tungsten, and volatilised platinum in quantity. A series of fifty of most batteries would have failed to have accomplished it. As a lighting agent for large or small lamps they stand unrivalled, whilst the absence of fumes allow of their presence in dwellings, conservatories, or places of a like nature. For driving motors one cell is usually sufficient, while, on the other hand, for electro-chemical demonstration three cells will be found sufficient for the entire work of a large laboratory.

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THE ATOMIC AND MOLECULAR SOLUTION-VOLUME.

By J. TRAUBE.

In connection with earlier communications I determined the specific gravities of a great number of solutions of salts—especially aqueous—by the pyknometric method. The directions given in my guide to "Physikalisch-chemische Methodon" (Physico-chemical Methods) were closely adhered to, and care was taken for the purity of the preparations.

These determinations of specific weights served for the calculation of the following values.

Let m be the molecular weight of a substance dissolved in water, *e g.*, the quantity of water which is contained in the solution for each mol. of the dissolved substance; d, the density of the solution referred to 4°; δ, the density of water as such. I then call the constant—

$$Vm = \frac{m + aq}{\alpha} - \frac{aq}{\delta},$$

the *molecular solution-volume* of the dissolved substance and the corresponding constant $V\alpha$ the *atomic solution-volume*.

The atomic and molecular solution-volumes would be equal to the atomic and molecular volumes of the dissolved substance if the density of the water as such were equal to the density of the water in the solution. On this in the sequel.

The molecular solution-volume is, in the first place, in the closest relation to the degree of electrolytic dissociation, or, as I shall call it, the degree of ionisation of the dissolved substances.

I still adhere to my former views as to the nature of ionisation, and I believe that the assumption of a far-reaching loosening of the ions in the dissolved mol. of an electrolyte agrees better with the facts than the assumption of complete disintegration of the molecule.

Whether, however, we select the point of view of the hypothesis of ionisation, or that of the electrolytic dissociation, is indifferent, but in any case either ionisation or electrolytic dissociation must be considered in calculating the molecular solution-volume. This done, only solutions of equal degree of ionisation were compared with each other, and where it was necessary observations of the congelation-point were effected.

In this manner numerous combinations of altogether 50 elements were compared together, and a series of simple relations of the atomic molecular solution-volumes were established.

A fuller account of this investigation will be given in the *Zeit. für Anorgan. Chemie.*

A comparison of the molecular solution-volumes of corresponding compounds leads to the following proposition.

The elements hydrogen, lithium, sodium, monovalent copper, silver, monovalent gold, and monovalent mercury have an equal atomic solution-volume.

In the series sodium, potassium, rubidium, cæsium, the atomic solution-volume increases with increasing atomic weight by a mean of 10 units of its value. The atomic solution-volume of rubidium is equal to that of ammonium.

Thallium compounds have a generally molecular solution-volume greater by some units than the corresponding potassium compounds.

The elements calcium, strontium, and lead have an equal or approximately equal solution-volume, also the elements zinc and magnesium, barium and cadmium, divalent iron and manganese, as also nickel and divalent copper.

Barium and cadmium have a decidedly greater atomic solution-volume than the first members of the corresponding triads. The volume of red cobalt is considerably greater than that of nickel. Glucinum has among the above divalent elements the highest atomic solution-volume.

The atomic solution-volume of trivalent iron seems equal to that of aluminium; the constant of chromium is apparently rather smaller.

The *green* chromium compounds have a decidedly smaller solution-volume than the violet compounds of the same metal.

Molybdenum and tungsten have an equal atomic solution-volume (molybdates, tungstates).

In the series of the non-metals there appeared the following regularities:—

Chlorine and bromine (in the chlorates and bromates) have an equal atomic solution-volume. Iodine (in the iodates) has a volume smaller by about 8·5 units. In the chlorides, bromides, and iodides, the molecular solution-volume of Cl : Br : I increases by 7·5 or 10 units.

The molecular solution-volumes of the perchlorates and permanganates are equal.

The atomic solution-volume of fluorine is smaller than that of chlorine by 16 units.

The same difference appears again for oxygen—sulphur, nitrogen—phosphorus.

In the series, sulphur, selenium, tellurium, phosphorus, arsenic, antimony, silicon, titanium, zirconium, the atomic solution-volume increases with the increasing atomic weight. The differences amount to 7—9 units. Equal atomic solution-volumes appears in nitrogen and vanadium (nitrates, vanadiates), carbon and silicon (carbonates and silicates).

These are the most important regularities which have hitherto appeared.

Such compounds, however, have been left out of consideration in this exposition which are formed by the sole combination of kindred elements, *i.e.*, such as stand near each other in the series of electro-chemical tensions. For such compounds, and for the elements themselves, other relations come into force.

The difference of the molecular solution-volumes of $K_2SeO_3 - K2SO_3$; $K_2SeO_4 - K_2SO_4$ was as a mean $= 7·5$. On the contrary, instead of this increase a decrease of 10 units was determined from sulphur to selenium for aqueous solutions of sulphurous and selenious acids. The difference $KBr - KCl$ was $= 7·5$; $CaBr_2 - CaCl_2 =$ about 2·75; $AlBr_3 - AlCl_3 = 3·75$. On the contrary, this difference for $PBr_3 - PCl_3$ was $=$ about 2 units. The circumstance that the determinations here were effected in benzene did not come into consideration. Quite corresponding results were reached for the series phosphorus, arsenic, antimony, as also carbon and silicon, on a comparison of the chlorides.

It seems that for the combinations of electro-negative elements with each other there appear quite different volume relations than for the compounds of electro-negative with electro-positive elements.

The regularities observed hold good, as my experiments and calculations have shown, for the most different temperatures and solvents.

In dissolved substances in the state of dilute solutions, crystalline water can be assumed either not at all or only exceptionally. In this respect I must modify a view which I have hitherto expressed. The molecular solution-volume is a strictly additive constant.

The difference Ag_2SO_4—Na_2SO_4—K_2SO_4 is very approximately equal to that of all other silver, sodium, and potassium compounds, the differences $K - \frac{1}{2}Mg - \frac{1}{2}Sr - \frac{1}{2}Ba$, &c., are in all corresponding compounds equal, or approximately equal, so that we are justified in establishing the following proposition:—For similar degrees of ionisation of a dissolved substance the influence exerted by a given ion upon the value of molecular solution-volume is approximately equal and independent of the other ion which is present with it in solution.

Most important is the question as to the relation of the atomic and molecular solution-volumes to the atomic and molecular volumes of the dissolved substances.

We can approach more nearly to this question if we compare the differences of the molecular-solution volumes with the differences of the molecular solution volumes calculated for the solid or the liquid state.

It appears that wherever regularities for the values of the molecular volume are established, the same differences may be calculated as for the molecular solution-volumes of the dissolved substances. That which is the *rule* for solid bodies or homogeneous liquids, is for dilute solutions the *law*. This is a theorem the significance of which will appear also in properties other than the molecular solution-volume, *e.g.*, the index of refraction.

The difference $\Delta\,vm$ for $K-Na$ is calculated for the dissolved condition generally as on an average = 10; the same difference reappears in a large number of potassium and sodium salts on comparing the molecular volumes of the solid compounds.

As for the dissolved condition in general, the difference in the solid state is in a number of cases $Ag-Na=0$, likewise $Pb-Ca-Sr$; $Mg-Zn$; $Mo-W$; also NO_3-Cl, $I-Br=10$; $Br-Cl=7{\cdot}5$, &c.

We cannot wonder that for the solid state there are only found regularities.

Disturbing influences come here into consideration.

The defectiveness of the determinations of the specific gravities; the circumstance that a body may have different specific gravities; the aggregation of molecules to greater complexes; the alteration of the specific gravities by crystalline water, and perhaps also the inaccurate selection of the temperatures of comparison. In consideration of these points it follows that the differences of the molecular solution-volumes are, in fact, to be regarded as the differences of the true molecular volumes, and that all the regularities deduced for the molecular and atomic solution-volumes are valid also for the molecular and atomic volumes.

That the values of the molecular solution-volume as such are not equal to the values of the molecular volumes of the dissolved substances follows from the circumstance that many of these values are vanishingly small and frequently even negative, at least at certain temperatures and in certain solvents. My earlier assumption of reducing negative character of the values to the formation of hydrates, I have been compelled to reject on account of the purely additive relation of the molecular solution-volume. Hence nothing is left but, in all such cases, to admit a contraction of the total water. That certain ions effect such a contraction, but others not, is *à priori* improbable; I incline therefore to the view that in all cases there occurs an attraction of water on the part of the dissolved ions the rather that such an assumption seems required for the total region of the organic substances.

As now in many cases, and especially on comparing kindred substances, the differences of molecular solution-volumes and molecular volumes are equal to each other, there follows the proposition:—Kindred ions exert, no matter with what other ions they are conjointly present in the solution, an equal attraction upon the solvent.

This proposition, which, in consideration of the above-mentioned disturbing influence in the determination of the molecular volume, may probably be generalised, extended to all ions and non-ionised molecules, seems to me of no small importance for the theory of osmotic pressure and of electrolytic dissociation. I purpose shortly returning to it in an especial memoir.

An Elementary Atom may occupy Different Spaces.

I call this property the *polysterism* of the elements.

A change of space occurs in most processes of reduction and oxidation, in the separations and the solutions of many metals, in processes of neutralisation, and wherever compounds of elements electro-chemically adjacent to each other pass into compounds of elements which occupy respectively remote places in the series of tension.

Polysterism is therefore important in the first place in various departments of chemical energetics, especially for thermo-chemistry and electro-chemistry.

Polysterism further takes us a step onwards in the theory of valence. The varying valence of an elementary atom is generally connected with a change of the atomic volume. This alteration of the state of the atom presents the possibility of understanding the non-constancy of the valence.

Occasionally polysterism becomes prominent without connection with any alteration of the valence. The change of colour of the chromium salts may be referred hither. I am also inclined to interpret the colour-phenomena of the cobalt salts and copper chloride in the same manner.

How far polysterism is otherwise of importance in deciding questions of isomerism must appear from future researches. The question must especially be raised if carbon is polysteric.

The regularities for molecular and atomic volumes observed are intimately connected with the isomorphism of the compounds; molecular volume and isomorphism more closely connected than it has been hitherto assumed. The small variations of molecular volume run in most cases parallel with the changes of form. The natural families of the elements which result on the basis of the relations of the molecular volumes generally coincide with the families which are established from the consideration of the crystalline forms. See the chapter on "Isomorphism," by Arzruni, in Landolt's new edition of Graham-Otto's text-book.

It must lastly be shown that the regularities here demonstrated demand attention, in as far as they in so many cases admit of calculations of specific gravities, sometimes of such accuracy that the calculation is preferable to observation. They are of value also as a check on the specific gravities of solutions hitherto published. The molecular solution volumes often explain various phenomena of solution, such as decomposition, formation of double salts, &c.

I propose to determine the molecular solution-volumes of organic substances, and I may already mention that here also the regularities for homogeneous substances discovered by Kopp appear far closer on observing the dilute solutions. A similar fact may certainly be expected for the indices of refraction. — *Berichte Deutsch. Chem. Gesellschaft*, xxvii., No. 18, p. 3173.

A CONSTANT ERROR IN THE DETERMINATION OF NITROGEN IN ORGANIC SUBSTANCES BY WEIGHING THE METALLIC PLATINUM REMAINING AFTER THE IGNITION OF AMMONIUM-PLATINO-CHLORIDE.

By Prof. Dr. L. L. de KONINCK.

The results obtained in the analysis are never calculated from the weight in vacuo, and to do this is, as a rule, needless, since the error arising = O if the material under analysis and the substance by the weighing of which the result is obtained have the same specific gravity. In most cases in practice we approach this condition sufficiently closely, so that the error occasioned may be disregarded. It is otherwise in the determination of nitrogen in organic substances, and even, though to a less extent, in ammoniacal salts and nitrates, if the proportion of nitrogen is found by weighing the platinum remaining from the ammonium platino-chloride.

Assuming that the specific gravity of the substance in question is 1·20, the true weight will be equal to this weight + the weight of the air displaced by the substance, and if we take the weight of a litre of air under the conditions prevalent at the time of weighing as 1·2 grms., the proportion of the real to the apparent weight will be 1·001 : 1·000. For platinum which has the specific gravity 21·5, the true weight approaches more closely to that found, and would correspond to the number obtained by multiplying the apparent weight by 1·00006. If we call the apparent weight of the substance as weighed in air P, and the weight of the platinum determined under the same conditions and remaining on igniting the ammonium platino-chloride as p, the proportion between platinum and the substance employed would be p/P, and would in reality be written as—

$$\frac{p \times 1\cdot00006}{P \times 1\cdot00100}.$$

According to this calculation the difference would amount to—

$$\frac{p}{P} \times 0\cdot00094,$$

or about 0·001, corresponding to an approximate quantity of 0·1 per cent. For a substance containing 10·0 per cent nitrogen we should find 10·01 per cent. This error is not considerable, but it requires to be taken into account when comparing the results obtained by different methods. An exact result can be obtained in such cases by deducting 0·1 from the percentage found.—*Chemiker Zeitung.*

THE DISTRIBUTION OF THE ORGANIC ELEMENTS.*

By Prof. W. PREYER, M.D., Ph.D.

The small number of the organic elements constantly excites anew the wonder of the naturalist. Only one-fifth part of all the known elements serves for the formation and the life of all animal, vegetable, and protistic beings, whether they are developed or rudimentary, healthy or diseased, great or small, common or rare. The compounds of merely 14 elements suffice for maintaining the entire immense fulness of life on the earth's surface. There are few facts which equally excite the wonder of the beholder of the inexhaustibility of the resources of living nature. It is certainly worth our while to consider the distribution and the properties of those privileged simple bodies, especially as it fosters our hope of throwing light from a new side into the obscurity of the greatest riddle—the mystery of life.

Firstly, the number of the organic elements. It is certain that from animals nothing can be obtained other than from plants, since the former are supported by the latter. All animals are either carnivorous or herbivorous, or both, *i.e.*, omnivorous; the carnivora feed upon the herbivora, so that ultimately all animals without exception feed from the vegetable world. The food of plants, contained in the air, the water, and the soil, must contain the same elements as the tissues of the plants themselves, since from the unchangeable character of every chemical element on the earth's surface nothing new can be produced.

Hence follows of absolute necessity that all the elements required for the support of animals—man included—must be contained in the food of plants. In fact during the last three decennia numerous and careful experiments have confirmed this weighty conclusion more and more firmly.

Many plants can grow, bloom, and fructify, if along with the ordinary atmospheric air they are supplied with a nutritive liquid containing water, saltpetre, gypsum, common salt, magnesium sulphate, calcium phosphate, along with traces of some soluble compound of iron, and traces of silicate and a fluoride.

Hence are, in fact, united all the organic elements and the compounds of the widest distribution. Paradoxical as it may sound, it is still true that the elements of these few compounds of the modest diet of plants are exactly the same as those of man's most sumptuous banquets. Again, we find these same elements in that nutriment which we all exclusively receive in the beginning of our life, *i.e.*, in milk. This alone, in truth the only complete food, is capable of supplying to the human body in its early development all the material required for its life, and in the most suitable form, just as the salts in the nutritive liquid of plants supply to it what it needs.

Entirely as plant-food differs from milk, or, indeed, from any human food, the elements of both are the same, in kind and number, as those of the maternal body producing the milk and that of the child, namely:—(1) Carbon, which the higher plants derive from the carbonic acid of the air. This carbonic acid they decompose under the action of solar light by means of the chlorophyll in their cells, and exhale at the same time oxygen. (2) Oxygen. This also is obtained by the plant from the air and from water, and at the same time (3) Hydrogen. There follows (4) Nitrogen; which plants chiefly obtain from saltpetre, *i.e.*, the nitrates of the alkaline metals, and also from ammonia. (5) Sulphur, which is obtained by the roots by decomposing the sulphates in the soil, namely, the sulphates of the alkaline and earthly-alkaline metals. (6) Phosphorus, derived from the alkaline and earthly phosphates. (7) Chlorine, required by many plants only in extremely small quantities, is obtained from potassium and sodium chlorides. (8, 9, 10, 11) Calcium, magnesium, potassium, and sodium, the last only in very minimum quantities, are supplied to plants of the soil in which they grow in the state of nitrates, phosphates, sulphates, and chlorides. (12) Iron, is supplied in water as carbonate, and perhaps as phosphate. Lastly (13), silicon is present in silicates and sand, and (14) fluorine in calcium fluoride and in the soluble alkaline fluorides.

Herewith the list of the universally distributed organic elements is exhausted. More than fourteen are not needed to form the nutriment of plants, and consequently that of animals. As both can contain nothing which is not introduced by the air inhaled and the food ingested, the above small catalogue includes all the indispensable organic elements. In them is bound up all bodily and spiritual life.

Meantime, a proposition of such scope requires other proofs before it can be fully accepted. Every given plant or animal, the diminutive egg of a parasite as well as the gigantic whale, a microscopic fungus as well as the tree to whose stem it adheres, a worm as well as a man, yield on chemical analysis always the above fourteen elements. These have truly so fundamental a significance for life, that where life is not one of them may be absent. Yet more; if the organism requires to maintain its vital activity in every direction, only the above fourteen elements—certainly in ever-varying combinations — no fifteenth or sixteenth can occur with equal universality.

What is the fruit of the empirical scrutiny? It is found in the first place that for ten of those fourteen elements their existence in every living being is placed beyond all doubt, namely, for carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, calcium, magnesium, potassium, and iron.

It is easy to demonstrate at any moment that every part of a living body contains carbon. If we dry and heat it, it blackens and is carbonised. The blackness is simply carbon, since if burnt alone in oxygen it yields only carbonic acid.

Hydrogen and oxygen must be present in mass in every living being, because each consists of water to two-thirds or four-fifths, or even nine-tenths. *Corpora non vivunt nisi humida.*

Nitrogen and sulphur are present without exception

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* A Discourse delivered before the General Meeting of the Nassau Association for Natural Science, at Wiesbaden, December 10th, 1893

since albumen contains both these elements, and there is no living tissue without albumen.

Phosphorus, calcium, magnesium, potassium, iron are always found in the ash of a plant or of the carcase of an animal, often most conveniently by means of the spectroscope.

All this is unquestionable. But in order to be sure of the presence of every such element in every plant we must not take too small a quantity for incineration, as otherwise the traces of iron might escape recognition.

Now for the four remaining elements. It has long been known that chlorine and sodium are present in every animal. Some botanists deny their presence in the higher plants. But whenever sufficient quantities of vegetable matter are burnt sodium chloride is found on the ash, even in parts remote from the sea.

The same applies to silicon and fluorine. Many plants flourish in nutrient liquids to which neither silicates nor fluorides have been added. But it does not follow that traces of these elements have not been introduced along with the other ingredients, or from the glass.

When I maintain that silicon and fluorine rank among the indispensable elements, I depend on the fact that fluorine occurs in the teeth, the bones, and the milk, and is one of the most widely distributed elements in the soil. Silica is always found in the ashes after the incineration of animal and vegetable matter.

(To be continued).

DETECTION OF SMALL QUANTITIES OF METALLIC SULPHIDES IN PRECIPITATED SULPHUR.

By R. FRESENIUS.

When in qualitative analyses a portion of the solution of a metallic salt acidified with hydrochloric acid and precipitated with sulphuretted hydrogen gives a white precipitate of sulphur, it is then permissible, in analyses where merely the detection of the metals is required, to infer the absence of metals of the fifth group (bismuth, cadmium, &c.) and such of the sixth group (arsenic, tin, &c). In accurate analyses such an analysis is not admissible, since the colour of very small quantities of cadmium, arsenic, and tin sulphide may be entirely masked by the joint presence of sulphur.

Such is the case if a coloured precipitate obtained with sulphuretted hydrogen from a solution acidified with hydrochloric acid is heated with ammonium sulphide or sodium sulphide, and a portion of the filtrate after dilution with water is mixed with hydrochloric acid. Here the white colour of the precipitate allows us to conclude the absence of large quantities of arsenic or tin, but very small quantities may still be present.

In the first or the second case it was therefore necessary in accurate analysis to wash out the precipitate, to treat it with one of the oxidising agents which dissolve metallic sulphides (hydrobromic acid, sodium peroxide, or the like), and to test the filtrate again with sulphuretted hydrogen after appropriate treatment, or to proceed with the precipitate as if it had been coloured.

The use of these circumstantial methods can in general be avoided in the following very simple manner.

A portion of the liquid containing the deposited sulphur is put in a small test-tube so as to occupy one-half. It is then covered with a layer of benzene or petroleum ether, about 2 c.m. in depth, closed with the thumb and shaken very strongly for one minute, and allowed to stand for a minute. If the white precipitate consisted merely of sulphur, it will have been dissolved in the benzene or petroleum ether, and we obtain two strata, the upper clear as water, and the lower slightly turbid. But if traces of a metallic sulphide were mixed with the sulphur they appear in the form of thin coloured films at the surface of contact of both layers, and the metallic sulphides which have remained undissolved generally coat the upper part of the test-tube above the level of the liquid with a slight faintly-coloured pellicle.

Only if such deposits are perceptible will it become necessary to have recourse to one of the two above-mentioned methods. In many cases it will be preferable to treat a larger part of the liquid in question like the small specimen just referred to, and to examine the sulphides. In this case, after the sulphur has subsided in the benzene or the petroleum ether, we filter through a wet filter, allow the aqueous solution to run off entirely, pour away the benzene or petroleum ether from the metallic sulphides which chiefly adhere to the filter, wash them with water.

I said above that my rapid process is in general available, because there are deposits of sulphur which do not dissolve in benzene or petroleum ether. Such are never obtained on adding hydrochloric acid to ammonium sulphide or sodium sulphide containing polysulphides, and very exceptionally on passing sulphuretted hydrogen into acid solutions, *e.g.*, on adding sulphuretted hydrogen to a liquid containing sulphurous or nitrous acid.—*Zeit. fur Anal. Chemie.*

ON SEPARATION OF METALS IN ALKALINE SOLUTION OF HYDROGEN PEROXIDE.

By P. JANNASCH and E. ROSE.

Separation of Bismuth and Zinc.

As initial material we used pure metallic bismuth and zinc. The amorphous zinc sulphate of commerce was found less useful, since, if dried in the air, or on long keeping, especially in summer, it lost water rapidly, and frequently gave too high results. The weighed quantities of the metals (from 0·3 to 0·45 grm. each) were covered with a little water and about 10 c.c. of strong nitric acid in a capacious porcelain capsule fitted with a handle. The solution obtained on heating was evaporated down and taken up again with 5 c.c. concentrated nitric acid and 50 c.c. of water. In another capsule we prepared at the same time a mixture of 25 c.c. of hydrogen peroxide at 3 to 4 per cent and 15 c.c. concentrated ammonia, and poured the zinc and bismuth solution, with constant stirring, into the alkaline oxidising liquid. It is quite essential to effect the precipitation in this manner, *i.e.*, in presence of a constant excess of ammonia. If this is not the case, as it would occur at first, if we poured the ammoniacal solution of hydrogen peroxide into the metallic solution, the precipitate of bismuth formed re-dissolves in the residual acid with a great loss of oxygen, and we have therefore at the conclusion of the precipitation no certain guarantee that we have really employed a sufficient excess of hydrogen peroxide. Further, after the neutralisation of the originally acid solution, the zinc will also be deposited at the same time, and only dissolves subsequently in the excess of ammonia, which, however, takes place slowly and imperfectly. These circumstances, which are opposed to an accurate separation, may be much more successfully avoided by the procedure above directed. The yellowish-grey flocculent precipitate produced (bismuth hydroperoxide) falls immediately to the bottom. After repeated stirring it is collected on a filter and washed at first with very dilute ammonia, and then with cold water, until a drop of the washings leaves no residue on evaporation. We then dissolved the precipitate on the filter with dilute nitric acid (1 : 4), using at most 10 c.c. of the acid measured, when concentrated, and the precipitation of the bismuth was repeated under the same conditions. For an ordinary analysis a single precipitation of the bismuth is sufficient, since the zinc is precipitated only in minimum traces which lie decidedly within the permissible limits of error. The precipitate of bismuth after filtration and washing was dried completely at from 90°—100°. It was then detached as completely as possible from the filter, which is cut carefully up into small pieces and transferred to a platinum crucible. This is then covered over and placed in a nickel beaker, which is also covered with an asbestos capsule, in order thus to effect a gradual incineration of the organic substance. Heat is applied by means of a so-called sieve-burner (Fletcher's pattern), to which gas is conveyed by two jets in order to enlarge the flame. It is first heated until the filter is carbonised, which generally requires from ten to fifteen minutes. The asbestos cover and the platinum lid are then removed, when in general the carbonised filter begins to smoulder. The flame is then from time to time removed from under the air-bath, and the glowing ash is cautiously fanned with the lid, and finally the process of oxidation is expedited as much as possible by stirring with a long platinum rod.

An absolutely complete combustion is, however, seldom effected, but small particles of carbon remain, which is unimportant. The residue in the crucible is moistened with concentrated nitric acid, evaporated to dryness on the water-bath, the main portion of the precipitate which has been previously set aside is added, and the crucible is again heated in the air-bath, which is entirely closed. In a short time everything is completely incinerated and oxidised, so that it can be without hesitation faintly heated and fused with the open gas-flame without the slightest injury to the platinum. The ignition and weighing of the bismuth oxide thus obtained are repeated in order to be certain of the constancy of its weight.

The weighings of bismuth give in the first place values slightly too high in consequence of the traces of silica, &c., contained in commercial hydrogen peroxide. A little silica can also be introduced at times from the ammonia and from the apparatus. It is therefore advisable, previous to the commencement of the operation, to determine the quantities of silica and alumina which may be contained in a large quantity of hydrogen peroxide. For this purpose we evaporate to dryness 50 c.c. of the hydrogen peroxide in a platinum capsule with the addition of a little nitric acid. In the best samples which we obtained, we found on the average in 50 c.c. 0·005 to 0·007 grm. silica, and 0·001 to 0·002 grm. alumina and magnesia. If we wish to determine the silica by itself in the weighed bismuth oxide, we dissolve it in nitric acid, evaporate the solution in a small platinum capsule until as dry as dust, re-dissolve the nitrate anew and filter off, taking the precaution to wash the undissolved flakes of silica continuously with warm dilute nitric acid.

We have ascertained by many experiments that the silica present in the hydrogen peroxide is carried down with absolute completeness, by the precipitation of the bismuth, but is as completely re-dissolved when the recent precipitate is again taken up in hot dilute nitric acid. The filters concerned yielded on combustion only minimum traces of ash, whilst the solution of bismuth contained, in fact, the silica in question.

The ammoniacal filtrate from the precipitate of bismuth is evaporated to dryness in a deep capsule of Berlin porcelain, stirring diligently towards the conclusion, so as to leave a granular residue. It is then heated (after the removal of the stirring rod) first for some time upon an air-bath, and lastly upon an asbestos capsule until the ammoniacal salts are completely expelled. A direct heating of the porcelain capsule with a free flame is to be avoided to prevent the loss of the zinc salts; platinum capsules cannot be used for the expulsion of the zinc salts, since they are somewhat attacked, so that the precipitated zinc carbonate encloses platinum and then appears grey after ignition. The zinc nitrate remaining in the porcelain capsule is dissolved with water with the addition of a couple of drops of dilute nitric acid, freed from impurities by filtration, and the clear filtrate is precipitated as usual with sodium carbonate. The washed zinc carbonate is dried at about 100°, and the filter and the precipitate are ignited separately in a porcelain crucible. Any traces of silica, alumina, and ferric oxide may be removed by dissolving the ignited oxide in dilute acetic acid, the undissolved residue being weighed separately and deducted. Such impurities were met with only in exceptional cases. Even the purest salts of zinc may contain traces of iron.

Separation of Bismuth and Nickel.

The separation was effected exactly as directed for the separation of bismuth and zinc. In the precipitation of nickel after the previous expulsion of the free ammonia, the ammonium salts are either driven off by cautious heating, or they are disregarded, and the liquid is at once precipitated with an excess of sodium hydroxide.

Separation of Metals by Means of Ammonium Persulphate.

The authors feel themselves free to append a preliminary notice of separation of metals by precipitation as hyperhydroxide. We are not yet in a position to point out any advantage in this process.—*Berichte*, xxvii., p. 2227.

SOME RECENT CONTRIBUTIONS TO OUR KNOWLEDGE OF METALLIC REDUCING AGENTS.*

By H. F. KELLER.

In the extraction of metals from their oxygen compounds, carbon is certainly the most important and useful reducing agent. Its great affinity for oxygen is utilised in the manufacture of iron and steel; the commercial production of other useful metals, such as copper, lead, zinc, and tin, is accomplished, either directly or indirectly, with its aid; and under its influence even the energetic metals of the alkalis release their powerful grip upon oxygen. Contrasted with this, the use of other substances for the purpose of abstracting oxygen is almost insignificant. Is it surprising, therefore, that carbon is looked upon as the reducing agent *par excellence*, or that the very idea of reduction seems to us inseparably associated with this element?

But the reducing power of a substance depends, in a large measure, upon temperature. It is well known to chemists that, under certain conditions, many metals have affinities which are far more powerful than those of carbon. When we glance over the pages of our chemical text-books, we see described there numerous experiments based upon the superior combining power of iron, aluminium, zinc, magnesium, and the alkali metals. The great Swedish chemist who arranged the elements according to their supposed affinities in an electro chemical series, was among the first to employ the positive alkali metals for isolating and preparing other elements. His method consisted in decomposing the halogen compounds by means of potassium; and it was subsequently improved by Berzelius's distinguished disciple, Wöhler. With its aid the latter chemist not only succeeded in reducing for the first time those remarkable metals, aluminum and glucinum, but he also showed that *all* those metals, the oxides of which cannot be reduced by either carbon or hydrogen, may be obtained by the action of potassium upon their halogen compounds.

It must not be supposed, however, that the use of metals as reducing agents is confined to the laboratory and the lecture table. Practical applications of such reac-

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* *Journal of the Franklin Institute*, October, 1894.

tions may be less conspicuous, but they constitute, nevertheless, the basis of not a few important metallurgical processes. The "precipitation" of lead from its sulphide ores; the solution of silver by the nascent lead in the blast-furnace; the amalgamation of the same metal in the iron pan; Deville's process of extracting "silver out of clay," recently so greatly perfected by Castner and Netto—are they not essentially reductions by means of metals?

In view of the facts mentioned, it may appear strange that comparatively little progress was made for many years in the study of the reducing properties of metals. We can, however, satisfactorily account for this when we consider the great tendency of metals to form alloys; it is difficult, in many cases indeed impossible, to obtain products entirely free from the reducing metal, and it is also well known that even a trifling amount of such an impurity may seriously impair the valuable qualities of a metal. Another obstacle has been the high price of those metals, which, by reason of their more powerful affinities, could, with advantage, be substituted for carbon.

Recent improvements in the commercial production of some of these metals have partially removed the latter obstacle. Thanks to the rapid progress of electro-metallurgy, aluminum is now to be had for about half a dollar per pound; sodium, once a chemical curiosity, is manufactured on an enormous scale at a less cost even than aluminum; and magnesium, now successfully extracted from carnallite, is applied to a variety of technical uses.

The radical changes which have taken place in our views on chemical affinity, as a result of the study of thermo-chemical phenomena, and the theory that the properties of the elements are *periodic functions* of their atomic weights, have also largely contributed to awaken interest and activity in the subject of our discussion.

The remarkably high heats of formation of its oxide and chloride, as well as the great stability of these compounds, render the action of magnesium upon other oxides and chlorides particularly interesting. Clemens Winkler, of Freiberg, has presented us with a most careful and systematic investigation of the reducing action of this metal upon oxides, while Seubert and Schmidt have communicated a similar exhaustive study of its action upon chlorides.

In giving a brief résumé of the results obtained by these experimenters, I shall adhere to the order adopted by them. It is based upon the periodic system, and has the advantage of showing many interesting relations that might otherwise escape notice.

Group I.

Group I. embraces a main group consisting of lithium, sodium, potassium, rubidium, and cæsium, and a sub-group consisting of copper, silver, and gold.

Owing to the difficulty of obtaining the oxides of the alkali metals in a pure condition, the carbonates were employed. It was found that to ensure the best results three atoms of magnesium are required for every molecule of the carbonate, thus:—

$$\mathrm{Na_2CO_3+3Mg=3MgO+C+2Na.}$$

The carbon as well as the sodium are deprived of their oxygen. It was found that, with the exception of cæsium carbonate, the alkaline carbonates *suffer reduction* to the metallic state when heated with magnesium, but that the intensity of the reaction diminishes as the atomic weight of the metal increases. Lithium, *e.g.*, whose atomic weight is only seven, was reduced with explosive violence, the metal being completely vapourised, while the tube in which the reduction was effected was shattered to pieces; potassium (atomic weight 39) and rubidium (atomic weight 85), on the other hand, were reduced quickly and without notable vapourisation.

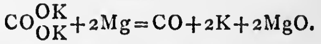
The reduction may be made in a tube of hard glass closed at one end; it is better observed, however, by conducting it in a current of hydrogen.

The preparation of potassium affords a most instructive experiment, which may well serve for lecture demonstration.

Into a wide tube of Bohemian glass a porcelain boat, containing about 2 grms. of the mixture of potassium carbonate, and magnesium is introduced. A current of perfectly dry hydrogen gas is passed through the tube, and the part of the tube surrounding the boat is gradually heated to incipient redness; the mass darkens, and upon further raising the temperature with the aid of the blast-lamp, the reduced potassium is completely expelled from the boat, exhibiting the deep green colour of its vapour, and is deposited in the form of a bright mirror in the cooler part of the tube. At the same time the hydrogen flame shows an intense violet colour. The dark residue remaining in the boat consists of magnesia and carbon. Enough potassium will have collected to show its colour, lustre; that it is sectile, fusible; its action upon water, bromine, &c.

In view of the high price of metallic potassium, the question as to whether the described reaction might not be carried out on the large scale suggested itself. Experiments showed, however, that in the absence of a gas current the distillation of the metal is very incomplete; and inasmuch as carbon monoxide forms an explosive compound with this metal, illuminating gas could not be substituted; in fact, the explosive carbonyl potassium was invariably formed when the quantity of magnesium present was insufficient for the *complete* reduction of the carbonate.

This was further proved by experiment. When two atoms only of magnesium were taken, the reaction took place according to the equation—



$$\mathrm{CO}^{\mathrm{OK}}_{\mathrm{OK}}\mathrm{+2Mg=CO+2K+2MgO.}$$

More promising results were obtained by employing potassium hydroxide instead of potassium carbonate. The danger of forming the explosive body is thus avoided, while the hydrogen gas set free simultaneously with the potassium ensures the complete distillation of the latter—

$$\mathrm{KOH+Mg=K+H+MgO.}$$

The reaction is somewhat violent, but may be moderated by adding some inert substance, such as magnesia, or by using the magnesium in the form of lumps or bars.

Winkler says, "it does not seem unlikely that the manufacture of potassium could be carried out by means of the same apparatus and the same operations which C. Netto has so successfully employed in reducing caustic soda with carbon. Into a retort filled with bars of magnesium and heated to redness, melted potash would be allowed to flow in a continuous stream, while the escaping mixture of potassium vapour and hydrogen is being cooled."

Winkler figures the cost of a pound of potassium to be about 3 75 dollars; the metal is now quoted at 28 dollars.

Beketow, who had previously made use of the action of aluminum upon potassium hydroxide, obtained only one-half of the theoretical yield owing to the simultaneous formation of potassium aluminate.

The sub-group, consisting of the heavy metals copper, silver, and gold, exhibited the reverse behaviour; the reduction was more energetic the higher the atomic weight of the metal. A very *slight* deflagration accompanied the removal of oxygen from cuprous oxide, while silver oxide was reduced with *explosive violence*. Very curiously aurous oxide was not visibly affected by the magnesium. This is explained, however, by the fact that gold oxide splits up into its constituents considerably below the ignition-point of magnesium.

Group II.

The main group comprises glucinum, magnesium, calcium, strontium, and barium; and zinc, cadmium, and mercury constitute the sub-group.

These elements are bivalent, and the action of their oxides upon magnesium is therefore—

$$R''O+Mg=MgO+R''.$$

In some cases the *hydroxides* were also used.

Glucina was easily reduced by magnesium; the mass became slightly incandescent, but some unaltered oxide was found in the residue.

There was no action observed when a mixture of magnesium and magnesia was heated in hydrogen; the oxide remained in the boat, while the metal sublimed in beautiful crystals. The existence of Beetz's sub-oxide could not be confirmed.

No visible sign of chemical action occurred when lime and magnesium were heated together. The reduction proved, nevertheless, to be almost complete.

A slight incandescence attended the reduction of strontia, whilst barium oxide displayed an energetic action upon magnesium. In both cases the decomposition was apparently complete.

None of the alkaline earth metals were found to be volatile at the temperature of reduction.

The hydroxides were even more readily acted upon than the oxides; so striking and beautiful, indeed, were the phenomena observed in the cases of calcium hydroxide and strontium hydroxide that Winkler proposes to utilise them for lecture illustration and in pyrotechnics.

The reduction of the oxides belonging to the sub-group was very energetic, the resulting metals being vapourised completely. Cadmium oxide develops less energy than either zinc oxide or magnesium oxide.

Both in the main group and the sub-group, the maximum of chemical energy occurs in the second member.

(To be continued).

ON THE TECHNICAL ANALYSIS OF ASPHALTUM.*

By LAURA A. LINTON.

In the year 1837 J. B. Boussingault published his celebrated memoir on the "Composition of Bitumens." In the researches upon which this memoir was based he had discovered that certain bitumens yielded to one class of solvents a portion of their content, and to another class of solvents another portion of their constituent hydrocarbons. He called the first portion "Petrolene" and the second portion "Asphaltene" (*Annales de Chemie et de Physique*, lxiv., 191).

In 1827 (*Bull. Soc. Chim.*, xvii., 156) Le Bel and Muntz went over the same ground, and in 1883 Le Bel again went over it, adding a few facts in relation to other bitumens than those previously examined, but leaving the two substances, petrolene and asphaltene, practically where he found them (*Bull. Soc. Chim.*, l., 359).

In 1837 the conclusions based on chemical research were far less exact than at the present time, and Boussingault concluded that the substances, petrolene and asphaltene, were simple substances, and also that they were identical from whatever sources they were derived. In this conclusion Le Bel, in a measure, appears to coincide.

It, however, requires no argument to prove, to any one at all familiar with the subject, that petrolene is nothing but a name that covers a great variety of substances, radically unlike, that exist in different forms of bitumen and are only related, in this instance, as being held in solution by a certain limited number of menstrua, and which include the whole list of paraffines and iso-paraffines, the olefines, the benzenes, and additive benzenes, with many other less abundant and well-known substances.

Ethyl ether and so-called petroleum naphtha, which latter is an indefinite mixture of fluid paraffines and iso-paraffines of high specific gravity, are the solvents used; but no determination has been made as to the influence of proportion in the mixtures of the substances dissolved, or as to the relative solvent powers of the two menstrua upon the different constituents of these mixtures. In fact, petrolene is nothing but a name which at present covers a vast expanse of the unknown.

It can be safely said that probability favours the assumption that asphaltene is a little more definite; but no certainty attaches to the identity of asphaltene from different sources or of asphaltene dissolved by different menstrua.

Therefore, in a general way, it may be said that asphaltene is that portion of the different forms of bitumen that is soluble in carbon disulphide, chloroform, benzene, and a few other less well-known liquids, and is not soluble in the menstrua that dissolve petrolene.

As the bitumens examined by the French chemists above mentioned have never assumed commercial importance, the questions relating to petrolene and asphaltene have remained matters of scientific interest only. However, since asphalt paving has become a business involving the expenditure of large sums of money, these problems are beginning to assume a wide importance outside the laboratory of the chemist, and to demand from technologists very serious consideration. Within recent years large numbers of so-called analyses have been reported, which represent various attempts to determine and set forth the relative value of many samples and kinds of asphaltum that may or may not be suitable for the many uses to which asphaltum is applied, but more particularly with reference to street paving. Prominent among the chemists who have been more or less extensively engaged in these analyses of alphaltes, are Mr. Clifford Richardson, Dr. Henry Leffmann, Dr. Samuel P. Sadtler, and Dr. De Smedt.

A perusal of the numerous published reports of Mr. Richardson reveals the fact that in his tests the solvents used for the extraction of petrolene and asphaltene were petroleum ether and carbon disulphide, while Drs. Leffmann and Sadtler, in their investigations and tests of asphaltes, used alcohol—presumably ethyl-alcohol,—carbon disulphide, and ether, as shown by the report submitted to the Citizens' Municipal Association and the Trades League of Philadelphia.

Neither of these gentlemen describe any process or method employed in obtaining the results stated. It is hardly consistent with the nature of the reports that they should. Nor has Mr. Richardson, in an article published in the *Journal of Analytical and Applied Chemistry*, in the numbers for December, 1892, and January, 1893, given any detailed description of the process he employed in order to obtain the numerous results of analyses that he there uses.

But little satisfaction can be derived from consulting Allen's encyclopædic work, so exhaustive upon every subject relating to technical organic analysis ("Commercial Organic Analysis," by Alfred H. Allen, London, 1886, ii., 375, 376, 377).

We find therein the following statements and notes concerning the solvents and methods used in the analysis of asphaltes:—"For the determination of the *total bituminous matters* in asphalte rock and mixtures containing it, C. T. Kingzett extracts the air-dried sample with freshly distilled Russian oil of turpentine, evaporates (*Analyst*, viii., 4) the resultant solution, and weighs the residue. The matter insoluble in turpentine is washed with ether, the *calcium* and *magnesium* carbonates dissolved in hydrochloric acid, and the washed insoluble *siliceous matter* weighed."

"H. P. Cooper prefers carbon disulphide for dissolving out the bituminous matters from asphaltic mixtures."

Allen adds in a note, "The carbon disulphide employed for dissolving the bituminous matter must not contain free sulphur. It may be replaced by chloroform or

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* *Journal of the American Chemical Society*, xvi., No. 12.

benzene (coal tar naphtha). If the residue left after extraction be dark coloured, foreign organic matters of valueless nature are present. Their proportion may be determined by igniting the weighed residue left after dissolving out the asphaltum, re-carbonating it with ammonium carbonate, again gently heating it and re-weighing. The loss of weight is the amount of *non-bituminous* organic matter present. In the case of samples leaving a white residue after exhaustion with carbon disulphide, the bituminous matter may be simply and accurately ascertained from the loss on ignition, taking care to re carbonate the lime before weighing."

In another note, page 377, he says: "Five grms. of the finely divided sample were digested for one hour with 50 c.c. of petroleum spirit (sp. gr. 0·7), and the mixture frequently agitated. The liquid is then boiled for a short time, decanted, and the residue boiled with another quantity of 25 c.c. of petroleum spirit. This treatment is repeated eight or ten times until the exhaustion is complete."

"E. Davies (*Pharm. Journ.*, [3], xiv., 394) reports that none of the organic matter in Val de Travers asphalte is insoluble in petroleum spirit."

Now, when we take into consideration the fact that turpentine, carbon disulphide, ether, chloroform, and benzene have been used indiscriminately by chemists in the extraction of asphaltene, the question very naturally arises, are the results that have been and that are being obtained by these different methods of analysis strictly comparable—that is, are they convertible terms? Will the same asphalte treated with different solvents show in each case the same percentage composition? If not, then it is evident that asphalte taken from different localities and subjected to dissimilar methods of analysis, cannot yield results of any value so far as purposes of comparison are concerned. Then again, if turpentine, carbon disulphide, and chloroform give a different proportion of asphaltene in the same asphalte, it is just as evident that asphaltene, instead of being a definite chemical substance, is a mixture, which mixture would doubtless vary in different asphaltes.

It was for the purpose of determining whether petroleum ether (paraffines), California naphtha, and ethyl ether are interchangeable solvents of petrolene, and whether turpentine, carbon disulphide, and chloroform are interchangeable solvents of asphaltene, that the research, the results of which are here given, was undertaken. That a series of such tests, faithfully carried out, should lead to the establishment of a method of analysis applicable to all asphaltes, and, at the same time, reveal something regarding the real nature of petrolene and asphaltene, was inevitable.

The specimens analysed were furnished me by Prof. S. F. Peckham, chemist of the Union Oil Company of California, and were as follows:—

1. *Crude Trinidad Asphaltum.*—From the Warren-Scharf Asphalte Company, of New York City. This specimen contained little or no water, as for several months it had been broken in small pieces, and so had lost the water which this asphaltum generally contains.

2. *Cuban Asphalte.*—A commercial sample obtained in New York City.

3. *Kuban Residuum.*—An artificial asphalte obtained from the distillation of Kuban petroleum from the western extremity of the Caucasus Mountains, Russia.

4. *Egyptian Asphalte.*—An Assyrian asphalte taken from the Dead Sea and imported into Egypt. This specimen was obtained in New York City.

5. *Asphaltic Rock.*—From Val de Travers, Switzerland. This asphalte was a sample of natural rock obtained at the office of Wm. H. Delano, representative of the French Company in New York City.

6. *Seyssel Asphaltic Rock.* — From the well-known locality in eastern France, obtained from the same source as No. 5.

7. *Turrellite.*—From a deposit lately discovered in Uvalde County, Texas, consisting of a mass of sea-shells cemented together by bitumen into a solid rock mass. It occurs in a rock formation said to be of Jurassic age, in which formation the Val de Travers rock also occurs. This specimen was obtained from the office of the Lithocarbon Company of New York City.

8. *Kentucky Asphaltic Rock.*—Obtained from Marshall Morris, Esq., Louisville, Ky.

9. *An Asphaltic Mineral.*—Resembling Gilsonite; reported as coming from Utah.

10. *California Maltha.*—Taken from a well at Summerland, on the coast, near Santa Barbara.

11. *Asphaltum.*—From mines recently opened near Asphalto, Kern County, California, in the eastern foot hills of the Coast Range Mountains, about 30 miles west of Bakersfield.

12. *Asphaltic Sandstone.*—From San Luis Obispo, California.

13. *Asphaltum.*—Picked up on the beach at San Buena Ventura, California, washed in from the Santa Barbara channel.

14. *Asphaltum.* — From the Ojai ranch, Ventura County, California.

15. *Grahamite.*—A so-called asphaltum taken from a vein in Ritchie County, West Virginia.

16. A portion of a compressed brick made from the asphaltic rock taken from the Seyssel mines. Exhibited at the Columbian Exposition.

17. *Hard Artificial Asphalte.*—An asphaltic residue obtained from the distillation of petroleum obtained near Santa Paula, California. It is known in the refinery of the Union Oil Company, of California, as grade "B."

18. *Soft Artificial Asphalte.*—From the refinery of the Union Oil Company, of California, at Santa Paula. Grade "D."

19. *Asphaltic Pavement.* — Obtained from Franklin Avenue, Buffalo, N.Y. It was laid in 1878, of Trinidad asphalte, wax tailings, and very fine sand. It is remarkable as having been laid for 15 years with almost no need of repairs.

20. *Asphaltic Pavement.* — From Governor's Island, New York Harbour, laid within the Fort at an unknown date, but so old that it has begun to break up from natural causes. Obtained from J. A. W. Pine, of New York City.

21. *Dubb's Artificial Asphalte.*—A so-called asphaltum obtained in operating the Dubb's patent process for the manufacture of asphaltum by adding sulphur to hot Lima-tar, and thereby burning out the hydrogen. This is an asphalte only in name. The specimen was obtained from J. A. W. Pine, of New York City.

22. *Roofing Pitch.*—Obtained from the Mica Asphalte Company, of New York City.

23. *Pitch.*—Obtained as a residuum in the distillation of Scotch blast-furnace tar. This specimen was obtained from the same source as Nos. 20 and 21.

In making tests to determine the best method to be used in the analysis of asphaltes, the well-known Trinidad and Cuban asphaltes were used, and all analyses were made in duplicate. In the case of asphaltes rich in bituminous matter, about a half grm. of the material, finely powdered, was used, but in the case of asphaltes in which the mineral matter constituted a large proportion, the quantity was increased to several grms.

The sample was weighed in an Erlenmeyer flask and digested over night in about 50 c.c. of petroleum ether; in the morning the clear solution containing the dissolved petrolene was passed through a balanced filter, and a fresh portion of petroleum ether added to the contents of the flask. The second digestion was continued for two or three hours, when the solution, as before, was filtered off, and the process repeated until the whole of the petrolene had been removed. The contents of the flask were then thrown upon the filter and thoroughly washed with petroleum ether. Cold turpentine was then poured upon the filter in successive portions until the filtrate passed through colourless, when the assumption was made that all the asphaltene and consequently all the bituminous matter had been removed.

The remaining organic matter, not bituminous, was determined by difference, that is, the residue on the filter, after digestion in turpentine, was washed with ethyl alcohol, dried, and weighed, in order to determine the percentage of asphaltene, after which the residue was burned in a platinum crucible, the difference in weight representing the organic matter not bituminous.

The contents of the crucible were now purely inorganic, and, in the case of most alphaltes, the residuum was sand more or less coloured with iron.

The analysis of Trinidad asphalte under this treatment gave so low a percentage of asphaltene, and so large a proportion of organic matter not bitumen, that it was clearly evident that *cold* turpentine had not dissolved, and could not dissolve, all of the asphaltene.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, December 14th, 1894.

Prof. W. E. Ayrton and Mr. H. C. Haycraft communicated a paper on a "*Students' Simple Apparatus for Determining the Mechanical Equivalent of Heat.*"

Mr. Haycraft, who read the paper, explained that the object at which the authors had aimed was the construction of an apparatus which could be placed in the hands of junior students, and by means of which a result correct within one per cent could be obtained without the introduction of troublesome corrections. The method employed is the electrical one, und the measurements to be made are (*a*) the value of the constant current passed through the resistance, as given by a direct-reading am-meter; (*b*) the average value of the P.D. between the terminals of the resistance, as given by a direct-reading volt-meter; (*c*) the mass of water heated *plus* the water-equivalent of the containing vessel, resistance coil, and stirrer; (*d*) the rise of temperature of the water; (*e*) the time during which the current is passed. Of these the measurements (*a*), (*b*), (*c*) can be effected without the introduction of an error anything like as great as one per cent. The case of (*d*) and (*e*) is different. The rise of temperature, to be measured with accuracy, should be fairly considerable, and the same remark applies to the time of heating as measured by an ordinary stop-watch. At the same time, if these two quantities are made unduly great, there will be too great a ratio of heat lost to heat generated during the experiment. The authors consider that, with a given amount of electrical power available, the best conditions will be obtained by making the percentage accuracy of the temperature measurement, the percentage accuracy of the time measurement, and the percentage of generated heat lost by surface cooling, equal. Hence they determine the mass of water to be used, and the time of heating which may be expected to give the best results. The immersed conductor is a strip of manganin about 0·25 inch wide, 0·03 inch thick, and 5 feet long, which is bent into a series of zigzags so as to form a kind of circular gridiron, the successive portions of strip lying all in one plane, aad the whole being held rigid by a strip of vulcanised fibre, to which each portion of the strip is screwed. Another precisely similar grid is placed 3 inches below the first, and the two are joined in series, and are mechanically connected together by thin vulcanite pillars. The water is contained in a glass beaker of just sufficient diameter to take the framework of manganin strip. This latter exposes a considerable surface (about 400 sq. c.m.) to the water, and is moved bodily up and down during the experiment, thus constituting an efficient stirrer. To allow sufficient freedom of movement, electrical connection is made by means of very flexible leads, each made up of about 210 thin copper wires. The results obtained by students for the heat-equivalent of the watt-second have an average deviation from the mean, if several experiments are made, of less than one-half per cent; and they agree with the best standard determinations within one per cent.

Mr. Griffiths thought it unadvisable to provide junior students with apparatus from which every source of error had been eliminated; they were thus led to underrate the difficulty of an experiment, and the care required to obtain reasonable accuracy.

Prof. Carey Foster agreed generally with Mr. Griffiths, and deprecated the use of direct-reading am-meters and volt-meters in experiments of this kind. He thought it preferable that a student should learn to reduce instrumental readings to absolute measure for himself.

Prof. S. P. Thompson dissented from the opinions expressed by the two previous speakers, and thought it was an advantage to students to have the use of direct-reading instruments.

Dr. Sumpner described a simple method which he had employed for measuring the mechanical equivalent of heat, and which depended on the heating of a stream of water as it flowed through a pipe containing the current conductor.

Prof. Rücker was inclined to take an intermediate view of the questions that had been raised. He thought that students should take for granted as little as possible concerning their instruments, but to verify every point, even if practicable, would occupy much time that might be otherwise more profitably employed.

Prof. Ayrton replied, and explained that the calibration of am-meters and volt-meters would be part of the work of a student at another part of his course.

A paper by Prof. Ayrton and Mr. E. A. Medley entitled "*Tests of Glow-lamps and Description of the Measuring Instruments Employed,*" was commenced by Mr. Medley, the latter part of the paper being held over till next meeting.

The object of the investigation was to find at what E.M.F. glow-lamps could be most economically run. Too low an E.M.F. gives a low efficiency, and too high an E.M.F. renders the lamps short-lived, so that there must be (for a given lamp) a certain E.M.F. which is more economical to work at than any other. It was also pointed out that, as glow-lamps deteriorate and become less efficient with use, it may be an economy to discard a lamp before the filament actually breaks. The lamp is then said to have reached the "smashing-point." Accumulators were used to drive the lamps, automatic apparatus being used to keep the E.M.F. constant, and when a lamp-filament broke, the fact was automatically recorded on a tell-tale.

NOTICES OF BOOKS.

Organic Chemistry. Part II. By W. H. Perkin, jun., Ph.D., F.R.S., Professor of Organic Chemistry in the Owens College, and F. Stanley Kipping, Ph.D., D.Sc., Lecturer and Assistant in the Chemical Research Laboratory, Central Technical College, City and Guilds of London Institute. London and Edinburgh: W. and R. Chambers, Limited, 1895. Small 8vo., pp. 552.

This work, along with Part I., which appeared previously, forms a very good introduction to the study of organic chemistry as at present understood. The present volume is mainly devoted to the aromatic compounds, but some of the concluding chapters are taken up with an account of the alkaloids and of dyes and their applications, and lastly of stereo-isomerism.

The concluding paragraph of this work refers to the use of a minute organism, *Penicillium glaucum*, in effecting organic separations. Perhaps this is the first dawn of a series of novel methods.

Indigo is here mentioned as a natural dye, the various syntheses by which it has been artificially produced, though of very great theoretical interest, being too expensive for practical purposes.

It is here mentioned that the sodium salt of indigodisulphonic acid, extensively used in dyeing, is known as "indigo carmine." This is certainly the case on the Continent, but British dyers cannot fortunately see the sense of giving the name of carmine to a blue colour.

This book will be an excellent guide for students intending to devote themselves to tinctorial chemistry. It may be advantageously used before entering upon works of a more special character.

Drs. Perkin and Kipping have presented the English-speaking chemical public with one of the best text-books of its class.

Elementary Qualitative Chemical Analysis: Adapted for Use in the Laboratories of Colleges and Schools. By Frank Clowes, D.Sc., and J. B. Coleman, F.I.C. London: J. and A. Churchill, 1894. Post 8vo., pp. 180.

This work is especially adapted for junior students and technical students rather than for such as take up chemistry from a professional point of view. We may, however, remark that the requirements of the technical chemist are in this country fixed at too low a standard. The less common metals are not taken into consideration, and the authors give no directions for the recognition of organic bodies. Blowpipe chemistry is not overlooked, but spectroscopic reactions are not mentioned.

The instructions given are clear, intelligible, and in accordance with our present state of chemical knowledge. For those whose time will not allow them to take a more thorough course, this work may be recommended.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 24, December 10, 1894.

At the meeting of the Academy the Perpetual Secretary made the official announcement of the death of Ferdinand de Lesseps, which took place at Chesnaye, in Indre, on December 7. The deceased had reached the age of 89 years.

Varieties of Graphite.—Henri Moissan.—Whatever variety of carbon may be taken for experiment, a sufficient rise of temperature always converts it into the state of graphite. This graphite may be either amorphous or crystalline; its density varies from 2·10 to 2·25. Its temperature of combustion in oxygen borders on 660°. There are several varieties of graphite, just as there exist several varieties of amorphous carbon and of diamond. The stability of graphite increases with the temperature to which it has been heated. This fact is shown by the greater or less resistance which graphite presents to conversion into graphitic oxide. In proportion as the melting-point of the metal increases, in which the graphite is produced, its difficulty of oxidation increases. It is thus that by a rise of temperature we may transform a graphite, easily attackable, like that of Ceylon, into a graphite much more resistant.

Phosphate from the "Grand Connetable."—A. Audouard.—The islet of Grand Connetable, situate at 27 miles to the east of Cayenne, possesses a very important deposit of aluminium phosphate. It is light, amorphous, and has been hitherto used only for the manufacture of alum. Its percentage composition is—

Phosphoric acid	39·10
Silicic "	1·70
Sulphuric "	0·06
Carbonic "	traces
Chlorine	traces
Alumina	25·59
Ferric oxide	8·03
Lime	1·40
Magnesia	traces
Water expelled at 105°	21·24
Water at redness	2·50
Not determined	0·38
	100·00

Its desiccation must be effected a little below 100°. It gives off nothing to cold water, but it is very soluble in acids and in ammonium citrate, and is hence readily assimilable.

On Pectose and on the Pectic Fermentation.—G. Bertrand and A. Mallèvre.—Pectase, though a ferment, is not alone able to coagulate pectine. It induces this transformation only in presence of a soluble salt of calcium, strontium, or barium. The precipitate formed under these conditions is not, as hitherto supposed, pectic acid, but an alkaline earthy pectate.

A New Procedure for Purifying Alcohols, Sugars, and other Organic Products.—E. Maumené.—This new procedure is the addition of potassium permanganate.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., Nos. 16 and 17.

This number contains an account of the life and researches of the late Jean Charles Galissard de Marignac, including a valuable list of his memoirs in the *Comptes Rendus*, in *Liebig's Annalen*, the *Journal fur Praktische Chemie*, the *Ann. der Chemie et Pharmacie*, the Chemical News, the *Phil. Mag.*, &c. Not a few of these papers are devoted to the rare earths and to the determination of atomic weights. This compilation is due to the persevering industry of M. E. Ador.

Study of certain Novel Phenomena of Fusion and Volatilisation produced by means of the Heat of the Electric Arc.—Henri Moissan.—Already inserted.

Chemical Classifications and Symbols in Antiquity and in the Middle Ages.—M. Berthelot.—The metals and their derivatives formed the basis of the earliest chemical classification. In contradistinction to them were two groups of substances, *spirits*, or volatile bodies, and *stones*, regarded as fixed and infusible. The discovery of sulphuric and nitric acids has been erroneously ascribed to the Arabs. According to authentic texts they were isolated and distinguished only after the 13th century, and their exact knowledge was only developed by degrees in the course of the 16th century. From this memoir it appears that chemistry took its rise, not in alchemy, but in technology.

Preparation of a "Sprouting" Variety of Graphite.—Henri Moissan.—The author has succeeded in preparing a variety of sprouting graphite analogous to that which occurs in nature. His methods are either the sudden cooling of cast-iron or the solution of carbon in platinum at high temperatures. The cause of the sprouting is a sudden liberation of gases.

New Experiments on the Reproduction of the Diamond.—Henri Moissan.—The author obtains a variety of carbon black or transparent. Some specimens have a distinct crystalline appearance, a specific gravity of from 3 to 3·5; they scratch ruby and resist twelve successive treatments with a mixture of dry potassium chlorate and fuming nitric acid. They burn in oxygen at a temperature of 900°, yielding about four times their weight of carbon dioxide. These properties are possessed solely by the diamond.

Some Observations on the Amidochromates.—G. Wyrouboff.—The author shows that the alleged amidochromates have no existence any more than the nitrochromates. He cautions young chemists not to rely on the purity of commercial products, but always to purify them before use.

Remarks on certain Hydrated Metallic Chlorides, with reference to a Paper by P. Sabatier.—H. Lescœur.—The writer's researches and those of Sabatier, though concerned with the same substances, are distinct. Sabatier has measured the calories of dissociation, and the author the tensions.

Preparation in the Electric Furnace of some Refractory Metals: Tungsten, Molybdenum, and Vanadium.—Henri Moissan.—Already inserted.

Certain Articles of Copper of very Ancient Date obtained from Chaldea.—M. Berthelot.—The objects found consist mainly of 77·7 per cent of copper, and are entirely free from tin, zinc, lead, iron, and silver. Hence they prove the existence of an age of copper preceding the age of bronze. They must have been made at an age anterior to 2000 B.C. At that date bronze and tin do not appear to have been wrought either in Chaldæa or in Egypt.

Certain Novel Objects of Copper from Ancient Egypt.—M. Berthelot.—The term bronze was used at one time by antiquarians and historians in a vague manner so as to include copper, brass, and bronze. In a similar manner *nitre*—a salt unknown in antiquity—has been used for *natron* and sodium sulphate or carbonate; sal-ammoniac was the name of a fixed salt, and *azur* served for cinnabar or vermilion.

Volatilisation of Silica and Zirconia, and on the Reduction of these Substances by Coke.—Henri Moissan.—Zirconia and silica melt rapidly in the electric furnace, and if the experiment is prolonged for seven or eight minutes, they boil and assume the gaseous condition.

Researches on the Iron of Ovifak.—Henri Moissan.—In certain specimens of the iron of Ovifak entrusted to us by Daubrée we have recognised distinctly in one sapphire, in three amorphous carbon, in two sprouting graphite, in one normal graphite, but in none of them diamonds, whether black or transparent.

Nitromethane and its Homologues.—MM. Berthelot and Matignon.—The nitro-derivatives of the formenic carbides are formed, setting out from nitric acid with liberation of heat comparable to that from nitrobenzene and its analogues. The greatness of this liberation explains the stability of these compounds and the fundamental difference of their reactions from those of the nitric ethers.

Propylene and Trimethylene Sulphates.—M. Berthelot.—A thermo-chemical paper not admitting of useful abstraction.

Reaction of the Alcohol Acids.—A. Berg.—Uffelmann has recently indicated for lactic acid a reagent obtained from a very dilute solution of ferric chloride so as to obtain a slight amethyst colour. This solution changes to a brilliant yellow under the influence of lactic acid. The author finds that this reaction is generally applicable to the acids possessing an alcoholic function, and that the phenol added to the ferric salt takes no part in the reaction. The reagent is best obtained by adding to 100 c.c. of distilled water two drops of ferric chloride at 45° B. and two drops of hydrochloric acid at 22° B. This reagent produces an intense yellow with the glycolic, lactic, α-oxyisobutyric, glyceric, gluconic, malic, tartaric, citric, mucic, and phenylglycolic acids.

Methyl and Ethyl Nitrosobutyrates.—G. Lepercq.—Not suitable for abstraction.

Action of Alkaline Nitrites upon α-Ethyl Bromopropionate.—G. Lepercq.—If we heat in the water-bath by cohobation the ethyl bromopropionate with its own weight of absolute alcohol and sodium nitrite, torrents of gas are evolved. If the liquid is poured into water, there is precipitated a reddish oil. This oil on purification becomes yellowish, and has the composition $C_{10}H_{16}N_2O_7$.

Action of Bromine upon the Oxide Ethers in Presence of Sulphur.—M. Genvresse.—The products of this reaction are alcoholic bromides and bromated aldehyds.

Various Notes.—E. Nægeli.—These notes treat of benzoyl anilide, of benzoyl chloride and aniline, of the behaviour of benzoic acid and aniline, of benzenylamidothiophenyl, of mononitrobenzenylamidothiophenyl, and of benzeneazophenol ethylate.

Researches on Phenylhydrazine. Action of Oxygen and of Water. Formation of Salts.—M. Berthelot.—A thermo-chemical paper not sufficiently important for insertion in full.

Action of Sulphuric Acid upon Camphene.—G. Bouchardat and J. Lafont.—The products of this reaction are the ether of the borneol of inactive camphene, the principal product; the sulphuric borneol acid yielding on further saponification borneol of inactive camphene and a small quantity of the polymers of camphene, the most abundant of which is $C_{40}H_{32}$.

A New Acid Isomeric with Campholic Acid.—M. Guerbet.—The composition of this acid is $C_{10}H_{18}O_2$. Its vapour density is 4·90, or by calculation 5·88. The acid is a colourless oily liquid which does not solidify at $-20°$. Its odour resembles that of valerianic acid. It boils at 180°—181°. At 0° its specific gravity is 0·9941; its rotatory power is $\alpha_D = +24° 38'$. It is almost insoluble in water, but miscible with alcohol and ether. It does not fix bromine. Unlike campholic acid, it behaves with coloured reagents like a strong acid. It is not precipitated from its alkaline solutions by carbonic acid. It is etherified at the ordinary temperature by the action of alcohol and hydrochloric acid, and the ether is saponifiable.

MEETINGS FOR THE WEEK.

Monday, 7th.—Royal, 4 30.
— Society of Chemical Industry, 8. (At Burlington House). "An Investigation of the Natural Solidified Sodium Sulphate Lakes of Wyoming, U.S.A." by Dr. D. Harvey Attfield, M.A.
Tuesday, 8th.—Royal Institution, 3. "The Working of an Electrical Current," by Prof. J. A. Fleming, F.R.S.
— Medical and Chirurgical, 8.30.
— Institute of Civil Engineers, 8.
— Photographic, 8.
Wednesday, 9th.—Geological, 8.
Thursday, 10th.—Institute of Electrical Engineers, 8.
— Mathematical, 8.
Friday, 11th.—Physical 5. "On the Passage of an Oscillator Wave-Train through a Plate of Conducting Dielectric," by G. U. Yule. "On the Heat of Vapourisation of certain Organic Liquids," by Prof. Ramsay, F.R.S., and Miss Dorothy Marshall, B.Sc. "The Thermal Conductivity and Emissivity of Brass in Absolute Measure, and the Influence of Curvature on Emissivity," by N. Eumorfopoulos, B.Sc. "Observations on Emissivity and Curvature," by A. W. Porter, B.Sc. "Experiments on the Production of Combination Tones," by Dr. C. V. Burton.
— Astronomical, 8.

TO CORRESPONDENTS.

Potassium Cyanide.—A correspondent wishes to know the names of manufacturers of cyanide of potassium 98/100 per cent.

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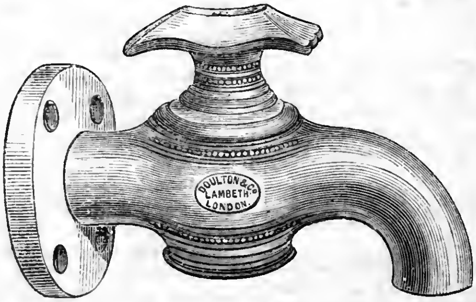

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January 4, 1895.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1833.

SULPHATE OF IRON AS A MANURE FOR POTATOES.

By E. WIGHTMAN BELL, F.C.S.

The use of sulphate of iron as a manure for certain crops has been advocated by several chemists, more especially by Dr. A. B. Griffiths, who has published many very satisfactory results from its use, particularly in the case of beans, turnips, potatoes, and clover. This opinion has, as a rule, been confirmed. Still, it was thought that further experiment on the subject might be useful.

The tables given below show the result of the addition of iron sulphate to other manures commonly used with potatoes. Each plot measured $\frac{1}{30}$th of an acre, and, as far as possible, under similar conditions as to weather, aspect, and composition of the soil (*i.e.*, all were in the same field). My thanks are due to Mr. T. Clayton, Spalding Marsh, for kindly allowing me to make the experiments on his land.

The soil is a rather heavy silt, and contains 4·54 per cent organic matter, 0·20 per cent phosphoric acid, and 4·22 per cent ferric oxide (only a very small quantity of which, however, is in a readily soluble condition).

The previous cropping was two years clover, the first crop being mown and the second eaten off by sheep each year. The clover was sown with wheat, which succeeded oats after mangolds. The whole of the plots were planted on the same day (April 4), and in very dry weather, and each received the same quantity of potatoes, which were "The Bruce."

Table I.—*Phosphates With and Without Iron Sulphate.*

No.	Manure per acre.	Yield per acre.
1.	3 cwt. mineral superphosphate	9 tons 11 cwt.
2.	The same, with ½ cwt. iron sulphate	11 tons 0 cwt.

The above shows an increase at the rate of 1 ton 9 cwt. per acre from the use of the iron salt.

Table II.—*Phosphates and Sulphate of Ammonia With and Without Iron.*

No.	Manure per acre.	Yield per acre.
3.	3 cwt. mineral superphosphate and 1 cwt. ammonium sulphate	10 tons 12 cwt.
4.	The same, with ½ cwt. iron sulphate	11 tons 7 cwt.

Showing an increase at the rate of 15 cwts. per acre on the plot manured with iron, which more than fifteen times repays the outlay on the iron salt.

According to analyses by Dr. Griffiths of the ashes of potatoes grown with and without sulphate of iron it would appear that iron has the power of replacing potash in plants so treated. The composition of the ash of the crops of potatoes was not ascertained, but it was found that kainit and superphosphate did not give as large a yield of tubers as super. and iron sulphate.

Plot 5.	3 cwt. mineral superphosphate and 1 cwt. kainit..	Yielded 8 tons 16 cwt.

In this case the addition of kainit has decreased the yield by super. only, by 15 cwts. (*vide* Plot 1), and is 2 tons 4 cwts. less than Plot 2. The reason for this diminished yield is not yet ascertained, but may probably be due to excess of saline matter, as it was found that the addition of either ammonium sulphate or iron sulphate further lowered the yield.

From the above results it seems that ferrous sulphate has a decidedly beneficial action on potatoes when used in conjunction with phosphates and ammonia.

NOTE ON THE

COMPARATIVE ANTISEPTIC ACTION OF THE PHENYL-SUBSTITUTED FATTY ACIDS.

By J. PARRY LAWS, F.I.C.

In the Thirteenth and Fourteenth "Annual Report of the Medical Officer to the Local Government Board," it has been shown by Dr. Klein and myself in experiments with phenol, phenolacetic acid, and phenolpropionic acid that the last-named had a more powerful antiseptic action on a pure culture of anthrax bacilli free from spores than phenylacetic acid, and that these acids were in turn much more powerful than phenol. I therefore thought that it would be interesting to ascertain whether the next higher member of this series of fatty acids, viz., phenylbutyric acid, possessed a more powerful action than phenylpropionic acid. In order to prepare phenylbutyric acid, I adopted, with slight modification, the process described by Fittig and Jayne (*Annalen Chem. Phys.*, ccxvi., p. 97). Instead of reducing the isophenylcrotonic acid with sodium amalgam, and carefully neutralising the alkali set free, it was reduced by heating with hydriodic acid (sp. gr. 1·7) and red phosphorus in a flask to which an inverted condenser was attached. Water was then added to the flask, and the contents filtered. The solid residue was dissolved in ammonia to separate the phosphorus, the acid re-precipitated from solution, and extracted with ether. The ethereal solution was dried, and the ether evaporated off. The acid distils about 280° C., and solidifies to a crystalline mass. When purified by crystallisation from water it softens at 48° C. and melts at 51° C. On analysis the following results were obtained:—

	Found.	Calculated for $C_{10}H_{12}O_2$.
Carbon	72·88	73·17
Hydrogen . ..	7·12	7·31

By using the above modification of Fittig and Jayne's process, a relatively much larger yield of the phenylbutyric acid is obtained. I take this opportunity of expressing my indebtedness to Mr. J. E. Marsh, M.A., for the valuable help that he gave me in the preparation of this acid in the chemical laboratory at Oxford.

There are two modes of action by which the influence of any given agent on the life and growth of a specific infective or septic micro-organism may be judged.

1. The restraining influence. 2. The killing power. The restraining influence of any substance is found by determining the smallest percentage of the agent which it is necessary to add to a favourable soil in order to prevent the development of the organism under observation. The killing power is found by determining the amount of substance it is necessary to dissolve in a liquid medium favourable to the growth of the organism, so that when the organism is sown in this mixture and transferred after a given time to a virgin soil its vitality may be so impaired that it is incapable of any development.

The following are the details of the experiments made to determine the restraining influence and killing power of phenylbutyric acid on sporeless anthrax bacilli. The cultivating medium being peptone broth and the temperature of incubation 35° C.

Restraining Influence.

Expt. I.—Solution containing 1 part of acid in 1000 of broth.

0·100 grm. in 100 c.c.

Five tubes inoculated with anthrax were sterile after six days.

Expt. II.—Solution containing 1 part of acid in 2000 of broth.

0·050 grm. in 100 c.c.

Five tubes inoculated with anthrax were sterile after six days.

Expt. III.—Solution containing 1 part of acid in 4000 of broth.

0·025 grm. in 100 c.c.

Five tubes inoculated with anthrax. After twenty-four hours two of the five tubes showed fair growth, the three remaining tubes showed copious growth after forty-eight hours.

Expt. IV.—Solution containing 1 part of acid in 3500 of broth.

0·0286 grm. in 100 c.c.

Five tubes inoculated with anthrax. All showed copious growth on second day; growth somewhat restrained for the first twenty-four hours.

Expt. V.—Solution containing 1 part of acid in 3000 of broth.

0·033 grm. in 100 c.c.

Five tubes inoculated with anthrax showed fair growth on second day.

Expt. VI.—Solution containing 1 part of acid in 2500 of broth.

0·040 grm. in 100 c.c.

Five tubes inoculated with anthrax. All five tubes sterile after five days' incubation.

Expt. VII.—Repetition of Experiment VI.

Five tubes inoculated with anthrax remained sterile after five days' incubation.

Killing Power.

In determining the filling power $\frac{1}{10}$ of a c.c. of a sporeless anthrax culture was mixed with 10 c.c. of peptone broth solution containing a known quantity of phenylbutyric acid. At intervals of five, ten, fifteen, twenty, and thirty minutes, minute quantities were transferred from this mixture to a suitable soil, to determine what effect the exposure to the antiseptic had produced upon the life of the organism.

Expt. I.—Solution containing 1 part of acid in 1000 of broth.

0·100 grm. in 100 c.c.

All the tubes inoculated at the above intervals with the exception of the thirty min. tube were fertile.

Expt. II.—Solution containing 1 part of acid in 500 of broth.

0·200 grm. in 100 c.c.

Five minutes' exposure to this strength was sufficient to kill the bacilli.

Expt. III.—Solution containing 1 part of acid in 650 of broth.

0·153 grm. in 100 c.c.

Only the tube inoculated after five minutes' exposure fertile, the remainder showed no sign of growth after prolonged incubation.

Expt. IV.—Solution containing 1 part of acid in 700 of broth.

0·143 grm. in 100 c.c.

Only the five minutes' tube fertile. The remaining tubes sterile after long incubation.

It will be seen from the above experiments that phenylbutyric acid restrains the growth of anthrax bacilli, when present in the proportion of 1—2500, and that it kills the *sporeless* bacilli when they are exposed for thirty minutes to a solution of 1 in 1000, or for ten minutes to a solution of 1 in 700.

In the following table I have compared the relative restraining and killing powers of phenol, phenylacetic, phenylpropionic, and phenylbutyric acids on anthrax bacilli:—

	Phenol.	Phenylacetic acid.	Phenylpropionic acid.	Phenylbutyric acid.
Restraining power ..	1—700	Not determined.	1—1900	1—2500
Killing power	1—200	1—450	1—600	1—1000
Length of exposure	45 mins.	30 mins.	30 mins.	30 mins.

It is interesting to note that the phenyl-substituted fatty acids increase in antiseptic power with the increase in the molecular weight of the acid, whereas Duggan (*American Chem. Journal*, vii., 62) has shown that in the fatty acids series itself the converse holds good, formic acid being more powerful than propionic acid in restraining the growth of *Bacillus subtilis*. His results are as follows:—

Formic acid	7 per cent.
Acetic acid	9 ,,
Propionic acid	12 ,,

These percentages almost exactly correspond to their relative molecular weights, and consequently to their relative saturating power of bases.—*Journal of Physiology*, xvii., No. 5.

EWART JOHNSTONE'S WAY TO PREPARE NITRIC OXIDE.

By MASUMI CHIKASHIGÉ.
Graduate of the Imperial University, Tōkyo, Japan.

In 1882, Dr. Ewart Johnstone announced in the Chemical News (vol. xlv., p. 159) that cobalt nitrate and potassium thiocyanate heated together readily yield nitric oxide. Except by Schertel in the Referate of the *Berichte of the German Chemical Society*, this announcement seems to have been received without criticism, and Michaelis inserted it in his edition of Graham Otto's "Inorganic Chemistry" among the methods of preparing nitric oxide.

The results of my own testing of the method oblige me to conclude that Johnstone is altogether wrong. We are directed by him to mix four parts of a solution of potassium thiocyanate with one part of a solution of cobalt nitrate, such as are ordinarily in use in the laboratory, and gently heat the mixture, when nitric oxide will be copiously evolved. An equation is given of the action, in which four molecules of the potassium salt and one of the cobalt salt appear, and since the quantities to be taken are so indefinitely set down, I started my experiments with these proportions of the salts, both practically in a state of purity. The result proved that in these proportions, as well as in many others which were tried, whether the solutions are dilute or concentrated, only gently heated or freely boiling, nitric oxide is not formed at all by them. Beyond the well-known fact that the mixed solutions are intensely green, no sign of any action was observed. When the solid salts, a little damp, were heated together, also as recommended by Johnstone, watery fusion occurred, and the water boiled off without gas being generated. When, however, the water being gone, the residue got much hotter, there occurred, as might have been anticipated, an explosive reaction in which torrents of gases escaped. These gases, collected over water, and gradually mixed with oxygen, proved to consist of nitric oxide to the extent of about two-thirds of their volume, the rest being principally nitrogen. Carbon dioxide and ammonia were also freely given off, and condensed together to form a sublimate, and a cloud, and a solution in the trough water, of ammonium carbonate or carbamate. The residue smelt strongly of ammonia and was black from the presence of cobalt sulphide, but did not contain the sulphur and the carbon which Johnstone supposed are formed, at least not in quantities which I could detect.

It is a matter of common experience that potassium thiocyanate boiled with dilute nitric acid is decomposed with evolution of nitric oxide and other gases, being partly oxidised and partly converted into the insoluble yellow perthiocyanogen. Now, only a small quantity, or rather only a weak concentration, of nitric acid is needed for this reaction, and the presence or absence of cobalt nitrate makes, I find, no difference. Probably, therefore, Johnstone's laboratory solution of the latter salt contained nitric acid in some quantity, as Schertel, indeed, has suggested.

DECOMPOSITION OF SULPHATES BY AMMONIUM CHLORIDE IN ANALYSIS ACCORDING TO FRESENIUS.

By MASUMI CHIKASHIGÉ.
Graduate of the Imperial University, Tōkyo, Japan.

The accuracy in all respects of Fresenius's standard treatises on Analysis is usually so unimpeachable that it seems proper to call attention to a misleading statement contained in a footnote to §153 A of the seventh and latest English edition of the "Quantitative Analysis," and also to be found in the earlier editions of this work (4th, 5th, 6th).

Having given in the text the method of separating from magnesium and alkali salts the small quantity of barium left in solution by ammonium carbonate, namely, by adding three or four drops of dilute sulphuric acid, Fresenius states in the footnote to it that the gentle ignition there directed to be made in order to expel ammonium salts, will also effect the removal of any small quantity of sulphuric acid which may remain after precipitating the barium. It is this statement which needs correction.

Even in § 68*a* and § 74*a* of the same work we find enough to cause us to doubt the accuracy of the later statement; for it is there mentioned that magnesium sulphate is not decomposed by igniting it with ammonium chloride, and, on the authority of Rose, that potassium and sodium sulphates, which are decomposable by this treatment, need, for it to be effective, its repeated application at a red heat, inducing effervescence. Obviously such ignition as this is not that gentle ignition directed to be used in § 153, and would entail serious loss of alkali chlorides by spirting and volatilisation. But to place the inaccuracy of the statement in the footnote beyond doubt, I have made a few simple trials of the method.

Magnesia, 0·5 grm., was dissolved in a little hydrochloric acid; to the solution were added two drops of dilute sulphuric acid (1 to 10 water by volume), a solution of about 2 grms. of ammonium chloride, and ammonia in small excess; and the whole was then evaporated to dryness, and all ammonium salts expelled at a barely red heat. Again, a solution of 2 grms. of ammonium chloride was added, and the evaporation and ignition repeated. The residue was dissolved in dilute hydrochloric acid and mixed with barium chloride, which gave a precipitate. On comparing this with that thrown down by barium chloride from two drops of the same dilute sulphuric acid in about the same volume of water, the ignited salts were found to have lost but very little, if any, of their sulphuric acid. The experiment was repeated three times with fresh magnesium chloride, and the same results obtained.

Similar experiments were made with sodium chloride, and no better removal of the sulphuric acid effected than when magnesium chloride was taken.

It is thus quite evident that other steps must be taken to remove sulphuric acid before it is allowable to calculate the weighed alkali salts as chlorides, or to resort to ways of separating magnesia from the alkalis which require the absence of sulphates.

ON THE ACTION OF HYDRAZINE UPON IMIDO-ETHERS.

By A. PINNER and N. CARO.

In two former communications there have been described the manifold, and in part unexpected, products which appear on the action of hydrazine upon benzimido-ether. It has been shown that, according to the proportions and the duration of the reaction occurring at common temperatures, there arise the three compounds—(1) benzenylhydrazine,—

$$C_6H_5.C\begin{smallmatrix}\nearrow NH\\ \searrow NH.NH_2\end{smallmatrix};$$

(2) dibenzylhydrazine; (3) diphenyldihydrotetrazin, which latter is oxidised by the oxygen of the air to the deeply-coloured diphenyltetrazin, which if boiled with acids is converted into diphenylisodihydrotetrazin and diphenylbiazoxol. Dibenzylhydrazidin is easily converted at common temperatures by the action of weak acids into diphenyltriazol, whilst ammonia is split off.

Benzenylhydrazidin is instantly converted by nitrous acid into diphenyltetrazotic acid.

The authors have, in a like manner, examined the products obtained by the action of hydrazin upon paratolenylimido-ether.

Among these are *p*-tolenylhydrazidin,—

$$C_7H_7.C\begin{smallmatrix}\nearrow NH\\ \searrow NH.NH_2\end{smallmatrix};$$

p-tolenylhydrazidin, with its carbonate, its picrate, and its nitrate.

With aldehyds, tolenylhydrazidine combines easily if its acid solution is heated with the aldehyd whilst water is split off.

Such a compound is benzylidentolenylhydrazidin.

If benzaldehyd is added to a solution of tolenylhydrazidin carbonate, mixed with a little soda-lye, and gently heated, there are formed white prisms of tolenylhydrazidin benzoate, $C_8H_{11}N_3.C_7H_6O_2+H_2O$.

Glyoxalen-ditolenylhydrazidine is formed as a hydrochlorate on boiling an acid hydrochloric solution of hydrazin with a solution of glyoxal-sodium bisulphite.

Nitrous acid acts upon tolenylhydrazidin as upon benzenylhydrazidin, forming instantly tolyltetrazotic acid in a theoretical proportion.

This is a powerful acid which readily decomposes the carbonates. Its salts with the alkalis and alkaline earths are easily soluble, but those with most of the heavy metals are insoluble.

The attempt was made to obtain with this acid an acetyl-compound by boiling with acetic anhydride. There was obtained, however, a mixture of acetyltolylamidine and ditolylmethylkyanidin. It is peculiar that diazobenzol chloride forms with tolenylhydrazidin not the diazobenzol-compound which was expected, but tetrazotic acid perfectly identical with that produced by nitrous acid.

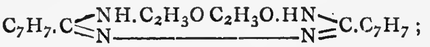
The authors have further obtained and studied benzoyltolenylhydrazidin, phenyltolyltriazol, toluyltolenylhydrazidin, and ditolenylhydrazidin. The last compound crystallises from spirit or from acetone in light yellow leaflets, and is insoluble in water and very difficultly soluble in hot spirit or in acetone.

Its hydrochlorate in a watery solution gradually gives off triazol.

The platinum double salt, $C_{16}H_{18}N_4.H_2PtCl_6$, is obtained by adding platinum chloride to a solution of hydrazin in cold dilute hydrochloric acid. It forms short yellow-red prisms which are completely decomposed if heated beyond 300°.

The double gold salt, $C_{16}H_{18}N_4 2HAuCl_4$, falls at once as a crystalline precipitate if gold chloride is added to a solution of hydrazin in dilute hydrochloric acid.

Diacetyl-ditolenylhydrazidine has the composition—



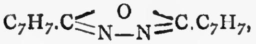
$$C_7H_7.C\begin{array}{l}\nearrow NH.C_2H_3O\ C_2H_3O.HN\searrow \\ \searrow N\text{——————————}N\nearrow\end{array}C.C_7H_7\ ;$$

it is formed by boiling a mixture of 1 part ditolenylhydrazidine, 3 parts dehydrated sodium acetate, and 15 parts acetic anhydride, for two hours in a reflux refrigerator, and adding water when cold.

The authors have examined the behaviour of this compound with nitrous acid, and obtained tolyltetrazotic acid, toluyltolenylhydrazidin hydrochlorate, and toluyl-nitrosotolenylhydrazidin hydrochlorate.

From ditolenylhydrazidin ditolyltriazol is easily obtained by the abscission of ammonia.

The authors have also prepared and examined ditolylazol silver, acetylditolyltriazol, ditolyldihydrotetrazin, ditolylisodihydrotetrazin with its double gold salt, ditolylbiazoxol—



$$C_7H_7.C\begin{array}{c}\nearrow \quad O \quad \searrow \\ \searrow N-N \nearrow\end{array}C.C_7H_7,$$

and ditolyltetrazin.

A CONTRIBUTION TO THE PHYSICS AND CHEMISTRY OF LIFE IN COLD-BLOODED ANIMALS.

By J. W. SLATER.

It is a fact admitted, but not, I submit, duly appreciated, that in the cold-blooded regions of the animal world we find more varied physical agencies and more multifarious and complicated chemical phenomena than in the hot-blooded forms, *i.e.*, the birds and the mammals.

No species in the two last-mentioned divisions has the power of emitting light, as is done by some fishes, many insects, and marine animalcules. No bird or mammal can use electric currents as weapons for defence or attack, as is done by several fishes, by a bug, and, it is said, by a slug.

Turning to chemical phenomena, we find numbers of arthropoda and a few mollusca endowed with the power of secreting and emitting silk. Nothing of the kind has been recognised among the hot-blooded tribes. Again, in reptiles, amphibia, fishes, insects, and arachnids we observe very generally the secretion of intense poisons, some rapidly fatal if introduced into the circulation of an enemy or a desired prey, and others dangerous only if the animal secreting them is ingested. One offensive poison only occurs in the higher ranks of life: the tarsial spurs of the male Ornithorhynchus are perforated for the emission of a secretion which is slightly venomous. But this can scarcely be called an exception, since the blood of the Ornithorhynchus is colder than the blood of the normal mammals by about 15° F. Neither does the virus of rabies form a true exception, since it is not a normal product but a pathological secretion.

Beautiful as are the colours of many birds, we find in them only one true dye or pigment, the touracine discovered by Prof. A. H. Church in the feathers of the plantain-eater of Africa.

On the contrary, in cold-blooded animals, such as mollusca and insects, dyes abound, and had not attention been drawn to a different quarter by the discovery of the coal-tar colours, they would have been more generally employed and studied.

Some colouring matters of the vegetable world pass over into the cold-blooded animals, but they extend no farther. Such are chlorophyll and tannin, which I have found in many insects, and which is probably the basis of the browns, drabs, greys, and other dull colours so common among Coleoptera. I noticed the occurrence of tannin in papers read before the Entomological Society, and reported in its *Transactions* (1887, p. 32). But I must not omit to state that a variety of tannin had been discovered as early as 1810 by Penant, of Bourgas, in a weevil, *Calandra granaria*, the well-known corn-weevil. As to the occurrence of alizarin in insects, I am doubtful.

As to odours, pleasant or offensive, we must admit that they are not wanting in warm-blooded animals. But among cold-blooded forms they are still more abundant and more striking. In certain groups of Coleoptera and Hemiptera their specific odours would be useful in the diagnosis of species, or at least of genera, had we a definite nomenclature for such phenomena.

The question now is whether the energy which in hot-blooded animals is expended in keeping up the temperature of the body is not in the cold-blooded forms converted into luminous or electrical or chemical energy? I would venture to recommend this as a sphere of research for chemists or biologists residing in climates richer in varied animal life.

THE DISTRIBUTION OF THE ORGANIC ELEMENTS.*

By Prof. W. PREYER, M.D., Ph.D.

(Continued from p. 6).

Whereby, except by means of plants in their foods, do fluorine and silicon arrive into the higher animals? The abundance of siliciferous animals (such as the siliceous sponges, &c.) in the sea is evidence of the biological importance of silicon. It serves for strengthening the frame work of animals and plants.

If we search for the presence of elements in living bodies other than the above fourteen, we meet with a great number which may be pronounced certainly absent in plants and animals in free nature. Here belong the heavy metals such as gold and silver, iridium and platinum, ruthenium and osmium, rhodium and palladium, as also the metals of the rare earths from Norway, such as erbium and terbium, samarium, gadolinium, scandium, and yttrium, and a long series of others. It is a matter of course that these elements like all others, as especially arsenic, can be introduced by man into his own body or into that of another animal, as often occurs in medical prescriptions, when *e.g.* preparations of bismuth or mercury are given; but this is here not the question. We must rather ask whether in the free course of nature other than the fourteen elements occur regularly in plants and animals. And this question must decidedly be answered in the affirmative.

Above all it is certain that copper is a constant ingredient of the blood of the Cephalopoda. Copper occurs also in the red pigment of the wing-feathers of the African Touracos and Musophagidæ. Zinc is regularly found in the so-called calamine violets and other plants near zinc works. Aluminium forms often a constituent of the ash of certain lycopods amounting to several per cents. Lithium has been found in tobacco, rubidium in tea and in beets, cæsium in oysters, boron in Italian grapes and melons, iodine and bromine in various marine plants, and manganese in certain muscles.

All these and others have been found not doubtfully but repeatedly, and that by good observers working independently of each other and at different places, probably

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* A Discourse delivered before the General Meeting of the Nassau Association for Natural Science, at Wiesbaden, December 10th 1893.

forming only the beginning of a series of similar facts which will be greatly multiplied in the future.

It would be important to know what is merely accidental in such puzzling occurrences of single elements outside the series in certain plants and animals. As the question now stands it can only be said that, beside the twelve to fourteen vital elements which are universally present in all living beings on the crust of the earth, there are some capable of distinguishing and selecting others which are very abundant or have been locally accumulated.

To these belong iodine, bromine, lithium, boron, zinc, cæsium, rubidium, copper, manganese, aluminium, and perhaps others which I do not mention, as their recognition is not certain.

Hence it appears suitable to separate all the elements contained in living beings into two groups. Those constantly occurring and indispensable are the elements of the first order; those which are not constant, though regularly present in certain vegetable and animal species, are the organic elements of the second order. On the other hand, the elements artificially introduced into the organisms for medical or experimental purposes, or which penetrate into the tissues like lead, tin, &c. (in certain occupations), do not rank among the organic elements, as little as the arsenic consumed by the Styrian arsenic-eaters.

For theoretical examination the elements of the first order are of incomparable greater significance than those of the second, since they are never wanting in living beings; but the collection of facts on the occurrence of other elements in the food of animals and plants is not to be neglected, since thereby our knowledge of the capabilities of living cells is greatly extended. And even if such an observation remains not understood for years or even decennia, its neglect is not admissible. In the meantime the elements of the first order must demand our attention.

What confers upon them the great pre-eminence above all the elements? What renders them alone serviceable for the maintainence of life in all parts of the earth?

More than twenty years ago I pointed out that they have all a small atomic weight. None of them exceeds 56 (iron). The figures are (omitting decimals):—

Hydrogen	1	Nitrogen	14
Carbon	12	Fluorine	19
Oxygen	16	Magnesium	24
Sodium	23	Phosphorus	31
Silicon	28	Chlorine	35
Sulphur	32	Calcium	40
Potassium	39	Iron	56

Hence the fourteen organic elements of the first order rank among the twenty-three elements which have the smallest atomic weights. The meaning of this fact appears at once if we consider that in equal quantities by weight of two kinds of food the greater number of atoms must occur where the constituents have the lowest atomic weights. In the chemism of life—as we shall show in future—the result depends on the effect of many atoms in the smallest space.

Further, the above named organic elements have all a remarkably low specific gravity. If we assign the greatest possible scope to sources of error and defects in the determinations, the specific gravities of the organic elements still remain the smallest, that is for the solid state, water being taken = 1; hydrogen, 0·62 to 0·73 (calculated); carbon, 1·3 to 3·6; nitrogen, 1·2 or slightly above (calculated); oxygen, slightly above 1·1 (calculated); fluorine, slightly above 1·0 (calculated); sodium, 0·97; magnesium, 1·7; silicon, 2·0 to 2·49; phosphorus, 1·82 to 2·34; sulphur, 1·9 to 2·1; chlorine, 1·8 (calculated); potassium, 0·86 to 0·88; calcium, 1·5 to 1·8; iron, 6·9 to 8·0.

Hence only iron, which occurs in living bodies merely in minimal traces, has a high specific gravity.

The meaning of this new fact of the low density of all other essential organic elements is close at hand. If the smallness of the atomic weights proves the great number of atoms in vital chemism, the smallness of the specific gravities points to the high number of molecules which come into action in equal weights. Life is movement and requires easily movable materials, especially gases. Life is metabolism. The most easily motile substances are those with the lowest atomic weight and the lowest specific gravity; consequently those most abundant at the surface of the earth and those most suitable for the maintenance of the vital chemical reactions. If some day the most organic elements became rare, all animals and plants would die of hunger.

The organic elements have further attributes which render them especially suitable for the maintenance of life. They have all a high specific heat, which, taking that of water as = 1, is included within the limits 0·10 and 0·46. That of hydrogen reaches 5·88, whilst all other elements have a specific heat of at most 0·10, and generally much lower down to 0·028.

From the high specific heat of all the organic elements, especially of hydrogen, it follows that all the essential constituents of the tissues of living organisms which are built up of such compounds must have a relatively high specific heat. This inference follows at once from their abundant proportion of water. The biological significance of this fact, as already remarked by Errera, must be sought herein, that living tissues when heat is conveyed to them easily indeed undergoes an increase of its intermolecular movements, but much less easily a rise of temperature than inorganic structures under similar conditions, *e.g.*, the noble metals.

As the constituents of living bodies are almost all bad conductors of heat, they cannot easily share rapid fluctuations of temperature in their immediate neighbourhood—the bark of a tree is a worse conductor than the wood,—and here lies a great advantage especially for all land animals and land plants, whilst in the sea the fluctuations of temperature upwards and downwards are less rapid, and take place within narrower limits than in the atmosphere. All life on the land and in the sea is, indeed, confined within such narrow limits of heat that at the change of the seasons, especially in the temperate zones, without the high specific heat of the organic elements and the small thermic conductivity of the tissues formed of them, many more small and minute organisms would yearly be destroyed by cold than now takes place in the winter.

Besides the physical properties so important for the vital process, the organic elements have further the chemical peculiarity of forming with each other the most numerous combinations and very large molecules, consisting of five, six, or even seven different elements. And these compounds are easily soluble and very readily decomposable, as *e.g.*, hæmatine, which contains in its crystals six elements.

The molecules of albumen, without which life is not conceivable, are very large and are easily decomposed. They are modified by the slighest influences.

This liability of the organic compounds in the living body is certainly the greatest obstacle to its explanation, but in a theoretical point of view it is the most important initial point of the biochemistry of the future.

If we represent to ourselves what, strictly speaking, is alive in the living body, we always arrive at the reply that only the cell contents, the protoplasm, lives, and different as are the opinions on its composition there is no longer any question that it is an extremely complicated structure, and not a "mucoid" or an "albumenoid" structure.

Protoplasm is continually decomposing as long as it is alive. The supply of the material used up in this self-consumption is yielded by the organic elements in the assimilable compounds of the food. But we must not imagine that the dissimilation of the entire series of the kataplastic chemical process ensue in the same manner as the imitations of the metabolic processes attempted in the laboratory. However many components of living animals and plants we produce by artificial synthesis, we have not proved even in a single case that the living body proceeds in the same manner. With decompositions the case is identical. How the organism forms the carbonic acid which it evolves is unknown, and yet there is absolutely no life without the formation of carbonic acid! The reason why this problem has not yet been found capable of solution lies doubtless in our insufficient knowledge of the nature of the place where the formation of carbonic acid takes place. That the foci of oxidation lie exclusively in the protoplasm is certain, but what is their aspect?

As protoplasm has an extremely complicated structure, recognised only of late since the improvement of the microscope, in which the very minute interstices and meshes, often at the very limit of visibility and not even permanent, but altering under the very eyes of the observer, the question arises whether in so peculiar a locality chemical reactions can altogether take place in the ordinary manner. An examination of the conditions necessary for the completion of any chemical reaction has shown that one of the most important of these conditions, the action of mass, cannot be realised in living protoplasm on account of the smallness of the open spaces. The chemical equilibrium can here be reached only to a very restricted extent. But then the chemism of the living cell-contents, the chemism of protoplasm, *i.e.*, the inter-reaction of the very unstable compounds of the organic elements, must be another, and lead to other results than in test-glasses and retorts. Even the extremely fine division of every minutest particle of nutriment which is burnt in millions and millions again of different places in the organism, and then especially the strikingly externally measurable average temperature of the focus of combustion, render it probable that, in the narrow interstices of living protoplasm, it is no longer the large molecules but the atoms which rush together in the moment of their liberation.

It is not the ordinary chemical reactions in which enormous numbers of molecules forming masses enter into action at the same place, but atomistic reactions which here come into play, single combats of atoms in the nascent state with strong unsatisfied affinities, and nowhere in an exactly identical manner, since the protoplasms, like organisms, are individually different.

Thus the more accurate determination of the properties of vital compounds of organic elements in connection with the scrutiny of the minutest structure of vegetable and animal protoplasm, promises to throw a clear light on the foundation of all life, the biochemical processes.

DISPLACEMENT OF CARBON BY BORON AND SILICON IN CAST-IRON DURING FUSION.

By HENRI MOISSAN.

The study of the solubility of carbon in different metals, or in the same metal at temperatures more and more elevated, has led us to examine what might be the action of boron and silicon on a given iron carbide maintained in the liquid state.

The action of boron upon iron has not yet been studied, or, at least, in the experiments made on this question the boron has not been detected after the experiment in the metal submitted to its action. As regards the action of silicon, no experiment has been conducted in a methodical manner. It has long been known in siderurgy that cast metals are the poorer in carbon the richer they are in silicon; but the action of silicon upon cast-iron has not yet been studied with precision.

Cast-iron in fusion is a liquid in which, as we are about to show, the reactions are sometimes as definite as in the aqueous solution treated in our laboratories at the ordinary temperature. The complexity of certain cast-irons which may contain a great number of compounds as impurities alone renders the reactions more complicated.

Action of Boron upon Grey Cast-Iron.—We set out with a grey cast metal from St. Chamond containing 3·8 of total carbon and 0·5 scoriæ. Ten grms. of this metal were placed in a lined porcelain boat with 2·5 grms. of boron. The whole was strongly heated in a reverberatory furnace in a porcelain tube filled with dry hydrogen. After the experiment we found in the boat a regulus well fused and covered with a black felt formed entirely of graphite. The metal had a yellowish tint, and presented on its surface some long prisms well crystallised. It contained 8 to 9 per cent boron. It was a borated cast metal mixed with iron boride partly crystallised.

This borated cast metal contained only 0·27 per cent of carbon, and gave no scoriæ on the combustion of the residue in oxygen.

Boron, therefore, easily combines with the impurities of the cast metal, and carries them off in the slags. With the iron oxide existing in solution in the metal it plays a part analogous to that which Troost and Hautefeuille have ascribed to manganese.

We may therefore conclude from this reaction that the boron has expelled the carbon in the proportion of 1 to 10, and at the same time eliminated the substances which form the slag.

This experiment was repeated four times with another specimen of grey cast metal from St. Chamond containing 3·24 carbon and 0·418 of scoriæ. After the action of the boron the following figures were obtained:—

	1.	2.	3.	4.
Carbon	0·36	0·28	0·17	0·14
Scoriæ	0·02	0·00	0·03	0·01

We then substituted a white refinery metal from the blast furnace of Saint-Louis, at Marseille. This cast metal contained 3·85 carbon and 0·36 of scoriæ. After the experiment it contained only 0·24 carbon and 0·06 scoriæ.

We have varied the form of the experiment, not allowing a great excess of boron to act upon the liquid metal. We melted at the forge 500 grms. of grey cast metal from St. Chamond, and when perfectly liquid we added 50 grms. of a borated cast metal containing 10 per cent of boron. After agitation the crucible was covered and the heating terminated. At the moment when the borated metal was added to the grey metal it remained for some time on the liquid bath and was dissolved only on agitation.

When cold the ingot obtained had a laminated aspect. It was very hard, resisting the graver, and having the appearance of a white casting.

By the action of boron the proportion of carbon in this metal was reduced from 3·75 to 2·83. The boron had therefore displaced carbon, a portion of which was recovered in the state of graphite between the metallic regulus and the crucible.

Displacement of Carbon by Silicon.—We repeated the same experiment, heating some fragments of grey cast metal in a lined boat with the powder of crystalline silicon. The silicon under these conditions expels the carbon, which is found as graphite above the metal. But, as we remarked at the outset, a cast metal produced in the blast furnace is a very complex compound.

We have repeated the experiment under more simple conditions.

We first prepared in the electric furnace a cast metal, rich in carbon, from soft iron and the charcoal of sugar. We then threw upon this liquid bath some grammes of melted silicon in globules. When cold the ingot, smooth on its upper surface, had the aspect of a silicated cast-iron with a white, brilliant fracture. It contained very little combined carbon and no graphite. But in the midst of the regulus there appeared a great cavity filled with graphite brilliant and well crystallised.

Conclusions.—Boron and silicon distinctly displace carbon in cast-iron or in melted iron carbide. These substances when maintained at a sufficient temperature behave exactly like aqueous solutions of certain compounds in which we can precipitate or displace this or that substance present in solution or combination.

If the displacement of carbon is not absolutely complete this fact is due to the formation of an equilibrium between the iron silicide and carbide, an equilibrium the conditions of which vary with the temperature and the impurities contained in the bath.—*Comptes Rendus*, cxix., No. 26.

SOME RECENT CONTRIBUTIONS TO OUR KNOWLEDGE OF METALLIC REDUCING AGENTS.*

By H. F. KELLER.

(Concluded from p. 9).

Group III.

THE main group embraces boron, aluminium (scandium), yttrium, lanthanum, and ytterbium, and gallium, indium, and thallium, form the sub-group. Three atoms of magnesium are required to abstract the oxygen from their oxides:—

$$R_2O_3+3Mg=3MgO+2R'''$$

Phipson has observed that boric acid is reduced upon ignition with magnesium. With the aid of magnesium, boron was also obtained by Geuther from the boro-sodium fluoride, and quite recently L. Gattermann has shown that boric acid as well as borax can be reduced by means of this metal, so as to yield products which are suitable for the preparation of various volatile boron compounds.

Winkler confirmed these observations. He states that the trioxide and the borate of sodium are easily reduced, the latter with much energy and evolution of sodium vapour. But he found that, instead of free boron, the residue contains magnesium boride of variable composition; for, on treatment with hydrochloric acid, boron hydride is given off as a gas. Sometimes a solid residue remains, which is likewise a compound of boron and hydrogen.

Owing to the acid-forming character of boron, the reduction was never complete; borates, upon which magnesium has no action, are always formed.

An attempt was also made to prepare a boron suboxide by limiting the supply of magnesium, thus:—

$$B_2O_3+Mg=2BO+MgO,$$

but no indication of such an oxide was observed.

A dark coloured product resulted from heating alumina with magnesium. The reaction appeared to be quite energetic; the mass exhibited a vivid glow and increased largely in volume. In addition to finely divided aluminum, a new oxide, AlO, and magnesium spinel had been formed. This monoxide could not be obtained in a pure condition, but its existence was proved beyond doubt. It is best prepared by heating in a current of hydrogen a mixture corresponding to—

$$Al_2O_3+Mg=2AlO+MgO.$$

This oxide is a brownish-black voluminous powder, is pyrophoric, and liberates hydrogen slowly from water; it precipitates cuprous oxide from copper sulphate solution, and is exceedingly susceptible to oxidation.

Winkler suggests that the blue colour of sapphire, and possibly also that of ultramarine, may be due to a small proportion of this monoxide.

Of the rare earths of group III., only yttria and lanthana were subjected to the action of magnesium. The energy of the reduction appeared to increase with the atomic weights.

Upon the oxides of the sub-group magnesium reacts with great violence; the intensity of reduction has its maximum in In_2O_3.

The behaviour of Tl_2O_3 towards magnesium appears to be an exception. Before the temperature of reduction is reached, this oxide splits up into Tl_2O and O_2, and the thallous oxide so formed is then only partially reduced. Thallium carbonate, however, is deprived of its oxygen completely, and with explosive violence.

Group IV.

The most interesting results perhaps were obtained in the fourth natural group of elements.

The known properties of carbon, silicon, titanium, zirconium, cerium, and thorium assign them positions in the main group, while germanium, tin, and lead constitute the sub-group.

In addition to their acid-forming dioxides, the majority of these elements are capable of giving monoxides. It was therefore deemed desirable to attempt not only the complete reduction of the higher oxides, but also a *partial* removal of the oxygen with a view to procure the lower oxides.

The statements of different experimenters concerning the action of carbon dioxide upon magnesium are somewhat conflicting.

That a ribbon of the metal will burn in an atmosphere of carbon dioxide was first observed by Kessler, but neither he nor other chemists who repeated and modified his experiment explained satisfactorily the nature of the reaction.

Winkler shows in the first place that magnesium, when *moderately* heated in a current of carbon dioxide, does not take fire, but is slowly converted at its surface into a carbide, carbon monoxide being formed at the same time. Upon increasing the heat to a full redness, the metal was inflamed and continued to burn with a dazzling light. The products of this combustion are magnesia and carbon.

When the magnesium is employed in the form of powder, these reactions take place even more readily. At a temperature considerably below a red heat carbon monoxide appears, and its quantity is greatly increased when low redness is reached. The metal burns with great brilliancy at a full red heat, and unless the current of carbon dioxide is very rapid, its reduction is complete.

It has already been mentioned that a separation of carbon was observed when magnesium acted upon carbonates; also that carbon monoxide was formed when an excess of the carbonate was present. Further experiments were made with calcium carbonate. A mixture of this substance with magnesium: $CaCO_3+3Mg=$ $=Ca+C+3MgO$, heated in a current of hydrogen detonated violently. The examination of the débris revealed the presence of a carbide of magnesium. No metallic calcium was observed in the residue when only two atoms of magnesium were used for each molecule of the carbonate.

According to Kessler burning magnesium is extinguished in carbon monoxide, while Parkinson asserts that at a red heat the metal burns vividly in this gas. Both observations were found to be correct. A spiral of magnesium wire ignited in the air, ceased to burn while introduced into a jar of carbon monoxide, but when strongly heated in a current of the gas the magnesium emitted light, and a grey coating of a carbide appeared on its surface.

Numerous experiments to determine the exact composition of this carbide were made, but without yielding a definite result.

Silicon exhibits a pronounced tendency to combine

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* *Journal of the Franklin Institute*, October, 1894.

with magnesium. Silicon-magnesium was first observed by Wöhler in 1858.

The reduction of silica by metallic magnesium was observed in 1864 by Phipson, and Parkinson showed in 1867 that silicon-magnesium, as well as a magnesium silicate, are formed at the same time. A few years ago L. Gattermann published an interesting paper in which he showed how very easily silicon dioxide is reduced by magnesium. He states that either silicon or silicon-magnesium can be obtained by varying the proportion of magnesium; and he applies the reaction to the preparation of volatile compounds of silicon, such as the chloride, bromide, iodide, silicoformic acid, silico-chloroform, &c.

Gattermann and Winkler agree that an energetic reaction occurs upon heating a mixture of one molecule of silica and two atoms of magnesium.

$$SiO_2+2Mg=Si+2MgO.$$

By adding magnesia to the mixture the heat of the reaction was moderated, but it was then found that much silicon-magnesium was contained in the product. If the reaction be effected at low temperature and in the presence of an excess of magnesium, silicon-magnesium is always formed, while at a high heat or in presence of magnesium, only amorphous silicon results.

A silicon monoxide could not be obtained by the reduction of silica, either by magnesium or silicon.

Many silicates are reduced quite as easily as the dioxide; in some cases the metallic base is likewise reduced, *e.g.*, potash glass.

None of the oxides studied presented greater difficulties than titanium dioxide. The results may thus be summed up:—Titanium dioxide was not reduced to the metallic state; a mixture of monoxide and a titanium spinel were the products of the reaction. Other intermediate oxides were sometimes formed. When the residue was treated with hydrochloric acid HTi_3O_4 was formed, which upon heating gave TiO_2 and hydrogen. Neither titanium-magnesium nor a titanium hydride was observed.

The reduction of zirconia was effected by heating it with magnesium to a high temperature. A monoxide could not be identified with certainty; and $ZrMg_2$ does not appear capable of existing.

According to the amount of magnesium employed either cerium or Ce_2O_3 were obtained from cerium dioxide. An intermediate monoxide was not formed. The reduction begins at a moderate red heat and is accompanied by a vivid glow. A considerable proportion of the magnesium is volatilised. In the nascent state cerium was found to absorb hydrogen in large quantities.

The formation of a metallic hydride at a bright red heat is a most remarkable observation. It is clearly proved to be correct by the following experiment.

A mixture is prepared according to the equation:—

$$CeO_2+2Mg=Ce+2MgO.$$

Twenty grms. of this mixture are placed in a combustion tube through which a current of dry hydrogen is passed, while a gentle heat is applied to expel any moisture. The further end of the tube is then closed with a strong clip. Hydrogen is allowed to enter the other end and the heat quickly raised to bright redness; a rapid current of hydrogen is seen to pass through the wash-bottles into the tube.

The hydride is of a brownish-red colour. It is without action on water at ordinary temperatures, but sets free hydrogen upon heating. Hydrochloric acid dissolves it to $CeCl_3$, with evolution of hydrogen. It was found impossible to completely remove magnesia from the product. The hydride is very inflammable, and detonates with potassium chlorate, potassium nitrate, &c.

The analytical results obtained point to the formula CeH_2.

After the existence of a cerium hydride had thus been established, the thought suggested itself that the other elements of group IV. might possibly be capable of forming similar compounds. Only carbon and silicon were known to form hydrides, but these elements could not be made to unite with hydrogen when their oxides were reduced by magnesium. Since titanium could not be reduced to the metal, it is not strange that all efforts to form a hydride gave negative results; zirconium and thorium did absorb hydrogen and yielded hydrides similar to CeH_2. The same was observed with lanthanum, and this led Winkler to believe that this element belongs to the cerium group; but he showed subsequently that yttrium and other trivalent elements, and even the divalent barium, strontium, and calcium can unite with hydrogen.

These hydrides represent a new class of metallic compounds, in which only half the usual valence of the metals is satisfied.

The action of magnesium upon chlorides has been made the subject of an elaborate research by Seubert and Schmidt.

I must content myself with a very brief statement of some of the main results obtained by these chemists.

Both the anhydrous bodies and the aqueous solutions of the chlorides were subjected to the action of magnesium.

In the former case the substance, either mixed with magnesium powder or conducted over it in the form of vapour, was heated to a high temperature. It was found that all chlorides could thus be reduced to the metallic state, but the reduction was incomplete in the groups of the metals of the alkalies and the metals of the alkaline earths.

In *neutral* aqueous solutions all the metallic chlorides, save those of the alkalies and those of the alkaline earths, gave up their chlorine to the magnesium. In some cases the metals were deposited in the metallic state (silver, gold, thallium, lead, arsenic, antimony), but in most cases hydroxides were precipitated. These hydroxides always represent the lowest state of oxidation. $CuCl_2$, *e.g.*, is changed into Cu_2O; chromium, aluminum, iron, manganese, cobalt, and nickel, all yielded hydroxides.

It would seem that the tendency to form such hydroxides is peculiar to the positive metals, and especially to those forming basic salts. Seubert and Schmidt believed this to be due to a dissociation of the chlorides into hydroxides and hydrochloric acid. They suppose, for instance, that an aqueous solution of $AlCl_3$ contains $Al(OH)_3.3HCl$. This view is rendered quite probable by the fact that solutions of copper, nickel, cobalt, and chromium exhibit the colour of their *hydrated* salts.

Of other metals whose oxides possess a high heat of formation aluminum has found some application in the reduction of oxides. Beketow has employed it with success to prepare some of the metals of the alkalis; and the experiments of Greene and Wahl of reducing manganese oxides by means of metallic aluminum are still fresh in our memory.

I am convinced that a continued study of the relative affinities of the metals for oxygen and other negative elements, will lead to important applications in metallurgy, and give new and valuable methods to synthetic and analytical chemistry.

Extraction of the Free Acids of Bees-wax.—T. Marie.—The purity of cerotic acid is ascertained by the following means:—Fractionated crystallisation of the acid in ordinary ether. Fractionated precipitations by magnesium acetate. Fractionated crystallisations of the methylic and ethylic ethers in ordinary ether. From the residue from the above treatment melissic acid is extracted by repeated treatments with methylic alcohol. Crude cerotic acid contains from 30 to 40 per cent of homologous acids.—*Bull. de la Soc. Chim. de Paris.*

ON THE TECHNICAL ANALYSIS OF ASPHALTUM.*

By LAURA A. LINTON.

(Concluded from p. 11).

A second set of experiments was then tried in which cold turpentine and carbon disulphide were used as solvents of asphaltene. The results obtained for samples 1 and 2 were as follows:—

No.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
1.	32·54	20·3435	12·368	34·6775	99·929
2.	25·049	54·53	2·441	17·9215	99·9415

The experiment was now made of somewhat varying the method of treatment for the following reasons:—First, because of the difficulty of dissolving out the asphaltene while on the filter by simply allowing the solvent to run through it, and secondly, because, in consequence of the high specific gravity of petroleum ether, a considerable portion of sand or other mineral matter mixed with asphaltene always adhered to the flask, thus necessitating a separate determination of this portion. The method now employed for the removal of petrolene and asphaltene was the decantation method, and the solvents used for asphaltene were hot turpentine and chloroform.

The samples were digested over-night in petroleum ether; in the morning the solution containing the petrolene was, as far as practicable, removed from the flask, and the remainder was evaporated over a steam bath; after weighing, the residuum containing the asphaltene was digested in hot turpentine over the steam-bath, and finally, the whole contents of the flask were poured upon a balanced filter and treated as in the first experiments.

The percentage composition of Nos. 1, 2, and 17, as determined by the decantation method, was as shown in the following table;—

No.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
1.	31·51	22·9865	11·4195	34·073	99·989
2.	25·055	52·245	5·758	16·918	99·962
17.	64·571	21·2545	13·706	0·3613	99·8928

In carrying out this method a great many determinations were lost, due to the fact that, in evaporation to dryness over the steam bath, the contents of the flask were in part bumped out. In consequence, this method was soon abandoned as impracticable, and finally, funnels with stop-cocks were employed, in which the contents of the filter could be digested. Boiling hot instead of cold turpentine was used, and when necessary the digestion was continued over-night, and all the after washings were made with hot turpentine. Numerous trials showed that carbon disulphide dissolves little more than hot turpentine. The last trace of asphaltene, insoluble in either turpentine or carbon disulphide, was removed by chloroform.

In order to determine the relative solvent power of hot turpentine, carbon disulphide, and chloroform, the following method of qualitative analysis was applied to the 23 samples enumerated above. From a half grm. to one grm. of the material was digested over night in a four-ounce Erlenmeyer flask with about 50 c.c. of petroleum ether. Next morning the contents of the flask were poured upon a filter, and the undissolved residue washed with petroleum ether until the filtrate was no longer coloured. Boiling spirits of turpentine was then poured upon the filter until it passed through colourless, when carbon disulphide was used in the same manner, followed lastly by chloroform. The action of the successive solvents is shown in the accompanying table (see next page).

Of the twenty-three asphaltes examined, there was not one that did not yield some asphaltene on treatment with chloroform; consequently, it is safe to infer that in the analysis of asphaltes, unless final washing be made with chloroform, the per cent of asphaltene will be too low. There was a marked difference observed in the different asphaltes as to the manner in which their constituent asphaltene was dissolved on treatment with hot turpentine. In Nos. 4, 5, 6, and 7, and a few others, the asphaltene dissolved out in a few minutes, while in the case of others, notably No. 15, it was a matter of hours, and even of days, before every trace soluble in turpentine could be removed. No. 9 seems to be an asphaltic freak, as it contains no petrolene whatever, and is insoluble in both hot turpentine and carbon disulphide, while chloroform and amylic alcohol dissolve but the slightest trace.

It was a difficult matter to determine the relative quantity of asphaltene dissolved by the different menstrua, as the only guide used was the colour of the filtrate. This suggests a most interesting research—the fractional, quantitative determination of asphaltene.

From my experience in the analysis of asphaltes, I would advise that a preliminary qualitative analysis be always made of each new variety of asphaltum before any quantitative determinations are attempted, care being taken to observe the behaviour of different asphaltes with the different solvents. This method of procedure is to be recommended, not only because it would prove an economy of time and reagents used, but also because, in this way, much would be learned concerning the nature of petrolene and asphaltene.

A trial was made with Cuban asphalte to determine the solvent power of petroleum ether (87° Beaumé) as compared, with that of California naphtha (74° Beaumé) and ethyl ether with the following results:—

Sample.	Solvent for Petrolene.	Per cent of Petrolene.
No. 2.	Petroleum ether	25·8516
,, ,,	California naphtha	32·444
,, ,,	Ethyl ether	32·5455

The high percentage of petrolene when California naphtha or ethyl ether are used indicates that the asphaltene is, in part, dissolved, and consequently, that these menstrua cannot be used as solvents of petrolene in the determination of asphaltes.

In selecting a method for the quantitative analysis based upon the results of these experiments, it is assumed that, until a strictly scientific method is worked out, the present empirical determination of petrolene and asphaltene will continue in use. The three considerations of economy, speed, and convenience will together control the selection. So long as the significance of the difference between the 25·8 per cent dissolved by petroleum ether and the 32·5 per cent dissolved by ethyl ether is an unknown element in the problem—that is, whether it be 7 per cent of petrolene or of asphaltene that is involved—it is better to use petroleum ether, because it is cheap and easily obtained of a uniform quality. So, too, it is better to use boiling hot turpentine followed by chloroform as solvents of asphaltene, and thus rid ourselves of carbon disulphide altogether.

With these considerations in view the following method of analysis is recommended:—

Weigh two suitable portions in 4-oz. Erlenmeyer flasks, and 50 c.c. of petroleum ether, cover, and allow to stand over night. The following morning decant the liquid upon a balanced filter placed within a 3-in. funnel provided with a stop-cock in the neck. Add another portion of petroleum ether to the flask, allowing two or three hours for digestion, and decant the liquid upon the same filter as before; this process is to be continued until the liquid ceases to be coloured, then transfer the whole of the bitumen to the filter. Dry the flask in a steam-bath and weigh; any increase in weight of the flask should be subtracted from the amount determined

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* *Journal of the American Chemical Society*, xvi., No. 12.

Sample No.	Hot Turpentine.	Carbon disulphide.	Chloroform.
1.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
2.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a perceptible amount.
3.	Dissolves nearly all.	Dissolves a trace.	Dissolves a trace.
4.	,, ,, ,,	Dissolves the slightest trace.	Dissolves the slightest trace.
5.	,, ,, ,,	Dissolves a trace.	Dissolves a perceptible amount.
6.	,, ,, ,,	,, ,,	,, ,, ,,
7.	,, ,, ,,	Dissolves the slightest trace.	Dissolves the slightest trace.
8.	,, ,, ,,	,, ,, ,,	Dissolves a trace.
9.	Dissolves nothing.	Dissolves nothing.	,, ,,
10.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
11.	,, ,, ,,	,, ,,	,, ,, ,,
12.	,, ,, ,,	,, ,,	,, ,, ,,
13.	,, ,, ,,	,, ,,	,, ,, ,,
14.	,, ,, ,,	,, ,,	,, ,, ,,
15.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.
16.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
17.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.
18.	,, ,, ,,	,, ,, ,,	,, ,, ,,
19.	Dissolves nearly all.	Dissolves a trace	Dissolves a perceptible amount.
20.	,, ,, ,,	,, ,,	,, ,, ,,
21.	,, ,, ,,	,, ,,	Dissolves a trace.
22.	Dissolves a large amount.	Dissolves a considerable amount.	,, ,,
23.	,, ,, ,,	,, ,, ,,	Dissolves a considerable amount.

as petrolene. Wash the filter and its contents with petroleum ether, place these with the filter counterpoise in a steam-bath, dry, and weigh; the loss in weight of the bitumen represents the petrolene.

Rinse the flask thoroughly with boiling turpentine and add the liquid to the filter in the closed funnel, pour upon the filter a sufficient quantity of boiling turpentine to wholly submerge it, cover and allow the digestion to continue for several hours or over night. Repeat the digesting and filtering with boiling turpentine until the filtrate becomes colourless. The filter should be much smaller than the funnel. Rinse the flask with chloroform and pour upon the filter, add sufficient chloroform to wholly submerge the filter and allow at least an hour for digestion; wash with chloroform until the filtrate passes through colourless, then dry and weigh; the loss in weight represents the asphaltene. The filter is now to be burned in a platinum crucible and, if the asphaltum be combined with limestone, the residue re-carbonated with ammonium carbonate, dried in a steam-bath, and weighed, the loss in weight represents the organic matter not bitumen, or coke, in the case of artificial asphaltic residuum, produced by heat.

There is necessity for washing the flask with the different solvents, not only because the petroleum ether is too light to rinse out all of the mineral matter, but also because some of the asphaltene adheres to the flask. Generally the turpentine removes all of the mineral matter, as well as part of the asphaltene, but if it does not, then after the flask is rinsed with chloroform it must be again dried and weighed, and the increase in weight added to the weight of the mineral matter in the platinum crucible. If water be present the asphalte should be dried in a steam-bath to a constant weight before being digested in petroleum ether. It is possible that some natural asphaltes might experience a trifling loss of volatile oils at the temperature of the steam-bath, but in most instances such loss would be too slight to be regarded. With care and patience this method has been found capable of yielding very closely concordant duplicate results at each step.

The table (see next col.) exhibits the results of a number of quantitative analyses made according to this method.

While this research is in no sense complete—it has, in fact, but opened up a wide field for further work—yet, sufficient evidence has been obtained to show that petrolene and asphaltene are not substances, but empirical terms that designate mixtures of substances soluble under certain conditions in different menstrua.

Sample. No.	Water.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
1.	2·029	32·4455	22·1115	8·1215	35·2865	99·994
2.	0·3911	25·4605	54·414	2·469	17·0305	99·7651
4.	—	35·087	63·183	1·7285	—	99·9985
				Not recarbonated.		
5.	—	8·518	3·924	25·791	61·764	99·997
6.	—	7·486	4·316	—	88·198	100·
7.	—	8·786	3·267	—	87·947	100·
8.	—	3·349	2·4215	—	94·228	99·9985
12.	0·335	11·323	3·81	1·124	83·407	99·999
15.	—	49·959	50·041	—	—	100·
17.	—	64·571	21·2545	13·706	0·3613	99·8928
18.	—	63·498	29·966	6·095	—	99·559
19.	—	4·387	2·831	4·102	88·65	99·97
20.	0·434	6·666	1·87	3·697	87·33	99·997
21.	—	66·788	31·932	1·278	—	99·998

It is not unfair to assume that in these empirical mixtures, so long known under the names of petrolene and asphaltene, the lower members of all the different groups of hydrocarbons now known may be found. Again,—just as some petroleums, which are varieties of bitumen, consist chiefly of paraffins—notably Pennsylvania petroleum—and some, like Russian petroleum, consist of the additive benzenes, while still others contain mixtures of the two, is it not reasonable to presume that solid bitumens, like liquid bitumens, are equally variable in composition? If this be the case, then it is equally fair to assume that any solvent taken will not dissolve substances of identical composition from different asphaltes.

A review of the results here given suggests the query, Have the methods heretofore employed for the technical analysis of asphaltum really been analytical at all? Would not a method and process suggested by the results of the qualitative analyses given in this paper and based on the successive application of different solvents and yielding results similar to those of fractional distillation really become analytical, especially if the separate portions dissolved by the different solvents were subjected to such treatment by oxidising agents as would enable us by a comparison of the products of oxidation to determine to what groups of hydrocarbons the different substances dissolved respectively belong?

I take pleasure in hereby acknowledging my indebtedness to the courtesy of the Hon. Thos. R. Bard, President of the Union Oil Co., of California, for the use of the laboratory of the company while engaged in this research.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 25, December 17, 1894.

The meeting of December 17th being the yearly public session of the Academy was taken up by the Presidential Address commemorating the discoveries of the year, and eulogising the members lost since the last annual session.

This discourse was followed by the announcement of the prizes awarded.

Half the Jecker Prize was awarded to M. Barbier for his numerous and important researches in organic chemistry. Portions of this prize have also been assigned to P. Adam and M. Meslans, the latter of whom has been successfully engaged in the study of the organic fluorides.

Two Montyon Prizes for protective improvements in the insalubrious arts have been awarded to A. Balland for his sanitary researches on wheats, flours, and bread, and M. Layet for his treatise on industrial hygiene.

The Cuvier Prize is this year awarded to John Murray, one of the naturalists of the *Challenger* Expedition, and the editor of its records.

A list was then given of the prizes offered for researches in future years. The Jecker Prize of 10,000 francs will be awarded next year for the most important progress in organic chemistry.

The Vaillant Prize for a study of the physical and chemical causes which determine the existence of the rotatory power in transparent bodies has been postponed to 1896.

A prize of 100,000 francs is offered for a remedy which will cure Asiatic cholera in an immense majority of cases, or for a detection of the causes of the disease, and for a certain prophylactic agent.

A general condition to be observed by all candidates for the prizes offered by the Academy is that the portion of their researches which they submit to the decision of the Academy must be sent in on or before June 1st of the year in which the prize is to be awarded.

Zeitschrift für Anorganische Chemie,
Vol. vii., Part 4.

Nitrogen Trioxide (Nitrous Anhydride).—G. Lunge and G. Porschnew.—The authors, briefly collating their results, conclude that nitrous anhydride is readily formed below −21° at the ordinary pressure from nitrogen peroxide and nitric oxide, and appears as a pure indigo-blue liquid. It is stable at the above temperature, but on a rise of temperature decomposition sets in and is completely or nearly complete on its passage into a state of vapour. The properties of the above mixture of components are, as regards any third substance, perfectly identical with those of N_2O_3 in a state of vapour.

Contributions to the Chemistry of Cerium.—L. M. Dennis and W. H. Magee.—Already inserted.

Simple Preparation of Hydrogen Phosphide.—J. W. Retgers.—If red phosphorus is placed in a glass tube and a current of dry hydrogen is allowed to pass over it, the gas escaping is merely pure hydrogen. But if the part of the tube where the phosphorus lies is heated with a gas flame, the bubbles of the gas, if allowed to escape through water, are found spontaneously inflammable.

Constitution of the Zeolites.—F. W. Clarke.—This paper does not admit of useful abstraction.

Part 5.

Constitution of the Cobalt, Chromium, and Rhodium Bases.—S. M. Jörgensen.—In this communication the author discusses the preparation and constitution of the aquotetramminxantho cobalt salts, and of those of the dinitrotriammin cobalt salts.

Double Chlorides and Bromides of Cæsium, Rubidium, Potassium, and Ammonium with Trivalent Iron, also a Description of two Ferro-ferric Double Bromides.—P. T. Waldon.—The ferro-ferric salts in question are—

$$RbBrFeBr_2.2FeBr_3 3H_2O$$
and $KBrFeBr_2 2FeBr_3.3H_2O$.

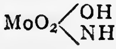
On Colloidal Silver.—E. A. Schneider.—Inserted in full.

On Solutions of Metallic Silver.—Carey Lea.—The results lead us to the view that the solutions of silver are colloidal. The solubility, however, is perfect, so that the solutions bore the same tests of solubility as the solutions of crystalloids.

Triammonium Orthophosphate and the Qualitative Detection of Magnesium.—P. Schottländer. If in testing a solution for magnesium we use ordinary ammonium phosphate (1 : 10) instead of sodium phosphate, we may, in the total absence of magnesium, obtain a finely crystalline precipitate which is deceptively similar to magnesium-ammonium phosphate, and may thus easily lead to error. This is especially the case if such ammonium chloride and strong ammonia have been added, additions well known for promoting the separation of magnesium.

Thorium Meta-oxide and its Hydrates.—James Locke.—The author concludes that the composition of meta thorium oxide corresponds to the formula Th_3O_5. The meta-thorium hydroxide has the composition $Th_3O_5H_2O$.

Molybdenum Amides.—Hermann Fleck and E. F. Smith.—The author recognises the existence of a monamide—



$$MoO_2\begin{cases}OH\\NH_2\end{cases}$$

The molybdenyl group (MoO_2) is evidently not capable of retaining two amido groups so as to form a stable product like $MoO_2(NH_2)_2$. Its existence, if at all possible, is of very brief duration. The same may be maintained of amido-molybdic acid, $MoO_3.OH.NH_2$.

Action of Phosphorus Trichloride upon Magnesium Nitride.—E. A. Schneider.—The possibility of producing a phosphorus nitride in a pyrogenous way seems not probable. The affinity of nitrogen to phosphorus at elevated temperatures is very slight.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 106.

This issue contains no chemical matter.

Royal Institution.—On Tuesday next (Jan. 15) Professor Charles Stewart, M.R.C.S., will deliver the first of a course of twelve lectures at the Royal Institution on "The Internal Framework of Plants and Animals." On Thursday (Jan. 17), Mr. William S. Lilly, M.A., will begin a course of lectures on "Four English Humourists of the Nineteenth Century"; and on Saturday (Jan. 19), Mr. Lewin F. Day will deliver the first of three lectures on "Stained Glass Windows and Painted Glass (from the Point of View of Art and Craftsmanship)." The Friday Evening Meetings of the Members will commence on January 18th, when a lecture will be delivered by Prof. Dewar on "Phosphorescence and Photographic Action at the Temperature of Boiling Liquid Air."

MISCELLANEOUS.

Determination of the Proportions of Calcium Carbonate and Magnesium Carbonate in Soils, Ashes, &c.—Albert Trubert.—We know that 1 c.c. of a normal solution of nitric acid or hydrochloric acid decomposes 50 m.grms. of calcium carbonate or 42 m.grms. of magnesium carbonate, setting at liberty 22 m.grms. of carbonic acid, occupying at 0°, and at the pressure of 750 the vol.—

$$\frac{22}{1{\cdot}977746} = 11{\cdot}12377 \text{ c.c.}$$

and forming at the same time nitrates or chlorides soluble in water. This reaction enables us to determine the total weight of the calcium and magnesium carbonates present in a given weight of earth, and consequently the weight of each carbonate. We attack a weight, p, of the dried earth with dilute hydrochloric acid, and find the volume V of the carbonic gas produced at the temperature t and the pressure H. We then calculate the corresponding volume V_0 of dry carbonic acid at 0° and at the pressure 760. On dividing V_0 by $11{\cdot}12377$, we obtain the number N of c.c. of the normal acid solution necessary to convert the insoluble carbonates entirely into soluble salts. We then take the same weight, p, of dry earth, and add N c.c. of the normal acid solution. We filter when there is no longer any further effervescence (the transformation is complete when a violet colouration is produced in presence of a drop of normal soda solution and of phenolphthalein). We wash the residue, dry completely, and weigh. Let p' be the weight obtained; the difference $p-p'$ gives the total weight p' of the carbonates contained in p of dry earth. We may thus calculate the proportions of calcium carbonate and magnesium carbonate. *First Method.*—Let x be the volume of carbonic acid at 0° and 760 produced by the unknown weight of calcium carbonate; let y be that produced by the magnesium carbonate. We have (1) $V_0 = x + y$. The weight of the calcium carbonate is in m.grms., $x \times 1{\cdot}977746 \times \frac{50}{22} = 4{\cdot}4948\ x$. That of the magnesium carbonate is $y \times 1{\cdot}977746 \times \frac{42}{22} = 3{\cdot}7756\ y$. We have then (2) $p_1 = x \times 4{\cdot}4948 + y \times 3{\cdot}7556$. If we replace y by its value taken from (1), we have—

$$x = \frac{p_1 - 3{\cdot}7756\ V_0}{0{\cdot}7192}.$$

Consequently the weight c of the calcium carbonate is (3) $c = 6{\cdot}2497\ p_1 - 23{\cdot}5963\ V_0$. We have then the weight m of magnesium carbonate by difference or by the formula $m = 23{\cdot}5963\ V_0 - 5{\cdot}2497\ p_1$.—*Comptes Rendus*, cxix., No. 24.

A Survival. — According to the *Chemiker Zeitung*, there exists—or did in 1890—the last of the alchemists, who, for a consideration in hard cash, is prepared to teach the art of converting copper into gold. In his letters, which are written in very bad German, the adept informs us that from 1 lb. of copper, new or old, he can produce 1 grm. of fine gold. The *Chemiker Zeitung* also calls attention to two new inventions for washing and bleaching, &c. "Polysulphine," the newest detergent, consists, according to Dr. Kreis, the chemist of the Canton Bâle, of—Water, 26·9 per cent; sodium carbonate, 70·5; sodium chloride, 0·55; combined sulphur, 0·59; free sulphur, 0·85. "Ammonin," placed on the market by a Heidelberg firm, as "crystalline ammonium sulphide," consists of the lime mud from the Leblanc soda manufacture, dried and ground! It is recommended by some disinterested experts as a "distinguished bleach and detergent."

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.

County Analyst.—Could you tell me what are the usual qualifications for a borough or county analyst, or for an analyst in a chemical works? I am anxious to commence a course of study with some such end in view.—W. D.

MEETINGS FOR THE WEEK.

Monday, 14th.—Society of Arts, 8. (Cantor Lectures). "The Arc Light," by Prof. Silvanus P. Thompson, F.R.S.
— Medical, 8.30.
Tuesday, 15th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
Wednesday, 16th.—Society of Arts, 8. "Commercial Synthesis of Illuminating Hydrocarbons," by Prof. Vivian B. Lewes.
— Meteorological, 8. (Anniversary).
— Microscopical, 8. (Anniversary).
Thursday, 17th.—Chemical, 8. "Acid Sulphate of Hydroxylamine," by Dr. Divers, F.R.S. "Mercury and Bismuth Hypophosphites," by S. Hada. "Kamala—Part III.," by A. G. Perkin.
— Royal Institution, 3. "Four English Humourists of the Nineteenth Century," by W. S. Lilly, M.A.
— Society of Arts, 4.30. The Lushais, and the Land they Live in," by Capt. John Shakespear.
— Royal Society Club, 6.30.
Friday, 18th.—Royal Institution, 9. "Phosphorescence and Photographic Action at the Temperature of Boiling Liquid Air," by Prof. Dewar, F.R.S.
— Quekett Club, 8.
Saturday, 19th.—Royal Institution, 3. "Stained Glass Windows and Painted Glass," by Lewis F. Day.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1834.

THE
COMMERCIAL SYNTHESIS OF ILLUMINATING HYDROCARBONS.*

By Professor VIVIAN B. LEWES,
Royal Naval College, Greenwich.

The two methods most used in chemical science for tracing the changes taking place in matter, and determining the composition of bodies, are, firstly, breaking up compounds into their ultimate constituents, a process which is called "analysis"; and, secondly, by building up the compound from the elementary matter which forms it, a process to which the name of "synthesis" has been given.

If we take chalk and heat it in the lime-kiln, or in the chemist's crucible, a heavy colourless gas, called carbon dioxide, escapes from it, and leaves behind a substance which we know as quicklime. If, now, this quicklime be further acted upon by chemical methods, the metal calcium and the elementary gas oxygen can be obtained from it, whilst the carbon dioxide when collected can be decomposed into the elements carbon and oxygen, and by such a series of operations as this we might perform the analysis of chalk.

If now we start with the metal calcium, with carbon, and with oxygen, it is perfectly simple to reverse the operation, and rebuild the chalk molecules from these elementary forms of matter; by burning the carbon and calcium respectively in oxygen, we obtain the quicklime and the carbon dioxide, and by bringing these substances together in the presence of moisture, chalk or calcic carbonate is once more formed, and we have synthetically built up the chalk from its constituents.

By such simple methods as these most inorganic compounds can be synthetically produced from elementary matter, but in the so-called organic chemistry it is not so easy to employ such constructive methods for the formation of compounds, and up to the end of the first quarter of this century it was supposed that organic bodies were only produced as the result of animal and vegetable life, and that their formation was due to the so-called "vital force," which was credited with governing all changes taking place in living organisms.

In 1828, Wöhler showed that urea could be formed from cyanate of ammonium, whilst, later on, Fownes made cyanogen by the direct combination of carbon and nitrogen, these two discoveries taken together proving the possibility of forming an organic product from inorganic materials, and after this point had been reached, and the possibility of applying synthetic methods to the production of organic bodies had been demonstrated, compound after compound was built up without the aid of either vegetable or animal life, and the barrier between inorganic and organic chemistry finally broken down. Cases, however, in which such methods could be commercially successful were few and far between, as in most cases the processes which had to be adopted were costly and laborious.

In all the phenomena of ordinary combustion which we employ to provide us with heat and light, there are no compounds of greater interest than the class of organic bodies which, being formed of carbon and hydrogen in various proportions, have been termed hydrocarbons, and it is to this class of bodies that all the gases which can be used as ordinary illuminants owe their luminosity. Amongst the hydrocarbons, the simplest compound is acetylene, in which two atoms of carbon are united with two atoms of hydrogen; and it has long been known that if a stream of hydrogen is passed through a globe in which the voltaic arc is produced between carbon points from a sufficiently powerful current, this gas is produced in minute quantities. It can also be formed in small quantities by the decomposition of carbon tetrachloride in the presence of hydrogen by the induction spark, whilst it is produced during processes of checked combustion in hydrocarbon flames.

The direct combination of carbon and hydrogen in the electric arc is a true case of synthesis, and if we could form acetylene in this way in sufficiently large quantities, it would be perfectly easy to build up from the acetylene the whole of the other hydrocarbons which can be used for illuminating purposes. For instance, if acetylene be passed through a tube heated to just visible redness, it is rapidly and readily converted into benzol; at a higher temperature naphthalene is produced, whilst by the action of nascent hydrogen on acetylene, ethylene and ethane can be built up. From the benzol we readily derive aniline, and the whole of that magnificent series of colouring matters which have gladdened the heart of the fair portion of the community during the past five-and-twenty years, whilst the ethylene produced from acetylene can be readily converted into ethyl alcohol, by consecutively treating it with sulphuric acid and water; and from the alcohol, again, an enormous number of other organic substances can be produced, so that acetylene can, without exaggeration, be looked upon as one of the great keystones of the organic edifice, and, given a cheap and easy method of preparing it, it is hardly possible to foresee the results which will be ultimately produced.

From acetylene we can produce all those bodies which we are accustomed to look upon as the most important ones in our coal-gas, and which, up to the present time, have never been produced from anything but coal, hydrocarbon oils, or other organic matter undergoing destructive distillation; but it has often occurred to those of us who are interested in the manufacture of illuminating gas, that as the supply of coal gets smaller, and as oil in time begins to share the same fate, from what sources are our illuminants and our fuels to be obtained; and in my mind, at any rate, the synthetic production of hydrocarbons has long been a day dream, which I, however, never expected to see possible on a commercial scale.

Not only was the synthetic production of acetylene in the electric arc well known, but ever since water-gas has been introduced, small traces of acetylene and methane have been found in it under conditions which render it impossible that they should have been produced from any compound present in the incandescent fuel, and which must have been due to the direct combination of carbon and hydrogen, but these traces only occurred in quantities so small as rarely to amount to one per cent, and it was manifest that the production of the compounds could not take place in large quantities under influences which would immediately tend to decompose them.

In 1836 it was found that when making potassium by distillation from potassic carbonate and carbon, small quantities of a by-product, consisting of a compound of potassium and carbon, was produced, and that this was decomposed by water with liberation of acetylene; whilst Wöhler, by fusing an alloy of zinc and calcium with carbon, made calcic carbide, and used it as a source from which to obtain acetylene by the action of water.

Nothing more was done until 1892, when Maquenne prepared barium carbide by heating at a high temperature a mixture of barium carbonate, powdered magnesium, and charcoal, the resulting mass evolving acetylene when treated with water; whilst, still later, Travers made calcic carbide by heating together calcic chloride, carbon, and sodium. None of these processes, however, gave any commercial promise, as the costly nature of the

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* A Paper read before the Society of Arts, Wednesday, Jan. 16, 1895.

potassium, sodium, or magnesium which had to be used made the acetylene produced from the carbide too expensive.

It is now some twenty-five years ago since I listened to one of the Friday evening lectures at the London Institution, given by Mr. Greville Williams, and in the same way that the thread of some melody lingers in one's mind, so has the concluding sentence of that lecture constantly recurred with ever-increasing force—"The impossible is a horizon which recedes as we advance; and the *terra incognita* of to-day will to-morrow be boldly mapped upon every schoolboy's chart"; and the haunting dream of the possibility of synthesising hydrocarbons commercially has, with the onward march of science, today become an accomplished fact.

As is so usual in the history of discovery, the factor which has endowed us with the power of doing this was not the outcome of an elaborate research, having this discovery for its ultimate goal, but was found by chance during the search for another object.

Whilst working with an electric furnace, and endeavouring by its aid to form an alloy of calcium from some of its compounds, Mr. T. L. Wilson noticed that a mixture containing lime and powdered anthracite, under the influence of the temperature of the arc, fused down to a heavy semi-metallic mass, which having been examined and found not to be the substance sought, was thrown into a bucket containing water, with the result that violent effervescence of the water marked the rapid evolution of a gas, the overwhelming odour of which enforced attention to its presence, and which, on the application of a light, burnt with a smoky but luminous flame.

Investigation into the cause of this phenomenon soon showed that in a properly constructed electric furnace, finely ground up chalk or lime, mixed with powdered carbon in any form, whether it were charcoal, anthracite, coke, coal, or graphite, can be fused with the formation of a compound known as calcic carbide, containing 40 parts by weight of the element calcium, the basis of lime, and 24 parts by weight of carbon, and that, on the addition to this of water, a double decomposition takes place, the oxygen of the water combining with the calcium of the calcic carbide to form calcic oxide or lime, whilst the hydrogen unites with the carbon of the calcic carbide to form acetylene, the cost of the gas so produced bringing it not only within the range of commercial possibilities for use *per se*, but also the building up from it of a host of other compounds, whilst the production of the calcic carbide from chalk and from any form of carbon renders us practically independent of coal and oil, and places in our hands the prime factor by which Nature in all probability produces those great underground storehouses of liquid fuel upon which the world is so largely drawing to-day.

Wonderfully and intensely interesting as is the train of thought opened up by the discovery of this substance and its commercial production, the object I have in view this evening is not to discuss theoretic possibilities, but to show you the important effect which it will have in the direction of our great gas industry, and the phase of this which I wish to deal with specially is the value of acetylene, either for producing *per se* an enormously high illuminating effect, or for the enrichment of low grade coal-gas.

When the calcic carbide is placed in a glass flask, and water allowed to slowly drip upon it from a dropping tube, the decomposition at once commences with considerable rapidity, and the acetylene pours off in a continuous stream. As the decomposition continues, the solid mass in the flask swells up, and is eventually converted into a mass of slaked lime.

Calcic carbide is a dark grey substance, having a sp. gr. of 2·262, and, when pure, a pound of it will yield on decomposition 5·3 cubic feet of acetylene. Unless, however, it is quite fresh, or means have been taken to carefully protect it from air, the outer surface gets slightly acted upon by atmospheric moisture, so that in practice the yield would not exceed 5 cubic feet. The density and hardness of the mass, however, protects it to a great extent from atmospheric action, so that in lumps it does not deteriorate as fast as would be expected, but in the powdered condition it is rapidly acted upon.

For commercial purposes the carbide will be cast direct from the electric furnace into rods or cylindrical cartridges, which, when 12 inches long and 1¼ inches in diameter, will weigh one pound and will give 5 cubic feet of gas.

The acetylene so made, when analysed by absorption with bromine, the analysis being also checked by determining the amount present by precipitation of silver acetylide, gives 98 per cent of acetylene and 2 per cent of air and traces of sulphuretted hydrogen, the presence of this impurity being due to traces of sulphate of lime—gypsum—in the chalk used for making it, and to pyrites in the coal employed.

Acetylene is a clear colourless gas with an intensely penetrating odour which somewhat resembles garlic, its strong smell being a very great safeguard in its use, as the smallest leakage would be at once detected; indeed, so pungent is this odour that it would be practically impossible to go into a room which contained any dangerous quantity of the gas.

This is an important point to remember, as the researches of Bistrow and Liebreich show that the gas is poisonous, combining with the hæmoglobin of the blood to form a compound similar to that produced by carbon monoxide, whilst the great danger of the latter gas is that having no smell its presence is not detected until symptoms of poisoning begin to show themselves, so that no fear need be apprehended of danger from this source with acetylene.

Acetylene is soluble in water and most other liquids, and at ordinary temperature and pressure—60° F. and 30 inches of mercury—ten volumes of water will absorb eleven volumes of the gas, but as soon as the gas is dissolved the water being saturated takes up no more. Water already saturated with coal-gas does not take up acetylene quite so readily, whilst the gas is practically insoluble in saturated brine—100 volumes of a saturated salt solution only dissolving 5 volumes of the gas. The gas is far more soluble in alcohol, which at normal temperature and pressure takes up six times its own volume of the acetylene, whilst 10 volumes of paraffin under the same conditions will absorb 26 volumes of the gas. It is a heavy gas, having a specific gravity of 0·91.

When a light is applied to acetylene it burns with a luminous and intensely smoky flame, and when a mixture of 1 volume of acetylene with 1 volume of air is ignited in a cylinder a dull red flame runs down the cylinder, leaving behind a mass of soot and throwing out a dense black smoke. When acetylene is mixed with 1·25 times its own volume of air, the mixture begins to be slightly explosive, the explosive violence increasing until it reaches a maximum with about twelve times its volume of air and gradually decreases in violence until, with a mixture of 1 volume of acetylene to 20 of air, it ceases to be explosive.

The gas can be condensed to a liquid by pressure, Andsell finding that it liquefied at a pressure of 21·5 atmospheres at a temperature of 0° C., whilst Cailletet found that at 1° C. it required a pressure of 48 atmospheres, the first-named pressure being probably about the correct one. The liquid so produced is mobile and highly refractive, and when sprayed into air the conversion of the liquid into the gaseous condition absorbs so much heat that some of the escaping liquid is converted into a snow-like solid which catches fire on applying a light to it, and burns until the solid is all converted into gas and is consumed.

In my researches upon the luminosity of flame, I have shown that all the hydrocarbons present in coal-gas and other luminous flames are converted by the baking action taking place in the inner non-luminous zone of the flame into acetylene before any luminosity is produced, and that it is the acetylene which, by its rapid decomposition at 1200° C., provides the luminous flame with these carbon particles, which, being heated to incandescence by various causes, endow the flame with the power of emitting light. The acetylene being in this way proved to be the cause of luminosity, one would expect that in this gas we have the most powerful of the gaseous hydrocarbon illuminants, and experiment at once shows that this is the case.

Owing to its intense richness it can only be consumed in small flat-flame burners, but under these conditions emits a light greater than that given by any other known gas, its illuminating value calculated to a consumption of 5 cubic feet an hour being no less than 240 candles.

Illuminating Power of Hydrocarbons for a Consumption of 5 cubic feet of Gas.

	Candles.
Methane	5·2
Ethane	35·7
Propane	56·7
Eythelene	70·0
Butylene	123·0
Acetylene	240·0

Having arrived at this startling result, it will be as well to at once turn to the commercial aspect of the problem, as it is upon this that the utilisation of this magnificent illuminant is entirely dependent. At the present time information from America shows that calcic carbide can be produced at a little under £4 a ton, and the beautifully pure lime obtained by the decomposition would be worth to the gas manager about 10s. a ton, and as a ton of the carbide will give rather more than 1¼ tons of quicklime or 1¾ tons of slaked lime, £3 10s. may be taken as the cost of the acetylene produced from a ton of the material, and will leave a margin for handling. A ton of the carbide will yield in practical working 11,000 cubic feet of acetylene, which will bring the cost of the gas out at 6s. 4½d. per 1000.

The cheapest and best enrichment process known at the present time is that introduced by Mr. Young, and which has been adopted at a number of gas works in Scotland and the north of England. In this process, by special methods of retorting, oils are decomposed to yield a rich gas, which, in the photometer, and burnt in suitable burners *per se*, gives an illuminating value of about 60 candles, but for which an enrichment value of 96 candles is claimed.

I am desirous of understating rather than overstating the powers of the acetylene, so that, instead of taking enrichment values for it which might be questioned, I prefer to simply take the illuminating power of the gas when burnt, *per se*, and the light measured in the photometer, which, as before stated, is 240 candles, whilst, for the same reason, we will take the claimed enrichment value of the Young gas instead of its photometric value.

An extended experience, gained with the Young process, as used at St. Helens for the enrichment of coal-gas, shows that the cost may be taken at 3s. 4d. per 1000 cubic feet. If now we compare this with the acetylene at 6s. 4½d. per 1000, we find that the 240-candle gas at this price would be equal to Young gas at 2s. 6½d. Moreover, the Young plant, to work a ton of oil per diem, costs —according to the experience at Peebles—£1500, and generates 22,000 cubic feet a day, the retorts for this purpose occupying a very considerable space, whilst, to make the same volume of acetylene, two tons of material would have to be handled, and the whole operation could easily be carried out in one small egg-ended boiler, fitted with an automatic water feed and automatic gas delivery valve to outlet of the main for the holder, so that the enriching gas could be added *pro rata* to the gas as it left the works in order to bring it up to any required strength in the same way as is done with the Maxim-Clarke enrichment, and all the troubles of stratification in the holder would be done away with. For the first few hours the water in the consumers' meters would absorb small quantities of the acetylene, but quickly becoming saturated, no further absorption would take place.

It is well known that acetylene forms two compounds with ammoniacal solutions of the metals silver and copper, and both of these compounds, when dry, can be readily exploded by percussion, friction, or heat. In the early days of gas supply copper pipes were used in New York, and Torrey in 1839 found in them a brown scaley deposit, which exploded when struck or heated to 200°C., and which was in all probability acetylide of copper.

An extended series of experiments on this point show that when metals are kept in the gas, even if moisture be present, no action takes places unless water condenses on the metal, when tarnishing with silver and copper, and to a less degree with brass, commences, and under these conditions an acetylide of mercury can also be formed, but the other metals remain unacted upon. If, therefore, iron, tin, lead, or compo pipes be used for the gas supply, no precautions are necessary. Copper and brass tubes must either be coated inside with some varnish not acted upon by the acetylene, or tin lined.

In America, which was the birthplace of this method of making calcic carbide, the acetylene is mixed with an equal volume of air, and the mixture burnt at small slit burners; but I confess to a grave mistrust of this method of using the gas, as the margin of safety in the amount of air required to convert the mixture into an explosive is so small that the danger of exceeding it on any large scale must be very great, as any mistake or alteration in the mixing apparatus used for this purpose might easily bring the percentage of air up to the explosive limit, whilst the diluting action of the nitrogen of the air reduces the illuminating value of the acetylene present from 240 candles to 130.

The possibility of liquefying acetylene by pressures not far exceeding those at which liquid carbon dioxide is produced so largely, enables enormous volumes of this gas to be compressed into the liquid state in small wrought iron or steel cylinders, and in this condition, by means of suitable reducing valves and burners of the right construction, it may be stored and burnt. Used in this way it will be of the greatest possible value for floating buoys, and the small cylinders can also be arranged in the form of portable lamps, whilst for use in the country, where no gas is available, a large cylinder of the liquid gas placed in an outhouse would supply a country house with light for a very long period; and there is no doubt that there is a very great field for it in this direction, as by utilising suitable burners a consumption of half a cubic foot an hour will give a light equal to from 20 to 25 candles.

Perhaps the most valuable suggestion which has been made with regard to the utilisation of this remarkable method of making acetylene is that advantage should be taken of the method of preparation to utilise the body for making portable lamps for dining and drawing-rooms in places where no gas supply exists. To do this a strong steel cylinder, 4 inches in diameter and 16 inches in length, is fitted with an opening in the top of such size that a pound cartridge or stick of the calcic carbide can be passed through it. The cylinder has a second opening at the bottom, closed by a screw, for cleaning out the lime left by the decomposition. The right proportion of water is put into the cylinder, and the stick of carbide, coated with a slowly soluble glaze, is inserted and the head of the lamp screwed on. This head contains a double reducing pressure valve, which brings down the pressure existing in the cylinder to that necessary for the proper consumption of the gas, it also being fitted with a valve. As the glaze dissolves from the surface of the stick of carbide, acetylene is generated, and the five cubic feet are compressed by their own pressure, the cylinder being stood in a vessel of cold water whilst the gas is generating, and the gas can then be burned from a suitable jet at the rate of half a cubic foot per hour, which will give a light of over 20 candles for something like ten hours. When the gas is all burnt out from the cylinder, the top of the lamp is screwed off, and the bottom plug also removed, and the lime washed out from the interior of the cylinder by a rapid stream of water, and re charged as before. Used in this way also, this gas would rapidly replace oil-gas for railway lighting, as the fittings at present in use for the Pope and Pintsch systems would answer perfectly well for the purpose of using acetylene, the only difference being that the cylinder placed below the carriage, which, under the present conditions, is filled with compressed oil-gas, would be utilised, not only as a storing, but as a generating vessel for the acetylene, the highly expensive oil-gas manufacturing and pumping plant being done away with, and a magnificent illumination ensured in the carriage.

Of late years an idea has been slowly permeating the minds of some gas managers in this country that it might be well to adopt a dual gas supply, one for fuel purposes, which would consist of a poor coal-gas of about 12 candles, whilst the gas for illuminating purposes would be of about 20 candles; and in one town at least it has been proposed and, I believe, carried out that a supply of poor quality coal-gas should be sent out during the day, when the maximum consumption is for heating purposes, and a richer gas at night for illuminating purposes, utilising the same mains for both. Although this is possible in a small town where the area to be supplied is not large, it would be impossible in a big town where many miles of huge mains have to be travelled before certain districts are reached, and the cost of a double set of mains would render a dual supply an impossibility.

The use of acetylene would render it possible for the gas company to send out a 12-candle gas for heating purposes, both by night and day, whilst a small enrichment cylinder might be attached to the gas outlet pipes from the consumer's meter, and which would be made to automatically enrich the gas supplied to his house, so that by setting a valve he could have any quality he might desire.

The economic value of an illuminant such as acetylene becomes apparent when we compare the cost of the gas for equal illumination with the light obtained from other illuminants. The London gas has an illuminating power of 16 candles, whilst the acetylene has an illuminating value of 240 candles, and this, at 6s. 9½d. per 1000, would in light-giving value be equivalent to London coal-gas at less than 6d. per 1000.

In order to obtain a given illumination, moreover, the volume of gas to be consumed is excessively small, as compared with any other illuminating gas, and the products of combustion are reduced to an excessively low limit. One hundred cubic feet of London coal-gas will yield 50 cubic feet of carbon dioxide and 140 cubic feet of water vapour as the products of its complete combustion, whilst 100 cubic feet of acetylene would yield 200 feet of carbon dioxide and 100 feet of water vapour. The acetylene, however, in its combustion gives a light of 240 candles, as against 16 yielded by the coal-gas; and for equal illumination, therefore, the amount of carbon dioxide and water vapour produced is enormously smaller.

The following table contrasts the products of combustion evolved from London coal-gas when consumed in various forms of burners, and giving an illumination of 48 candles, which may be presumed to be the amount of light required in a fair-sized London dining-room, and contrasted with this is the amount of the products of combustion which acetylene would evolve in giving the same amount of light; whilst to make the meaning clearer, I have added the number of adults who would exhale the same amount of carbon dioxide in the same time.

Burrer.	Gas consumed.	Carbon dioxide produced.	Adults.
Flat flame, No. 6 ..	19·2	10·1	16·8
Flat flame, No. 5 ..	22·9	12·1	20·1
Flat flame, No. 4 ..	25·3	13·4	22·3
London Argand ..	15·0	7·9	13·1
Acetylene..	1·0	2·0	3·6

If we obtained the same amount of light from paraffin lamps, the carbon dioxide evolved would be equivalent to 22·5 adults; whilst as far as carbon dioxide goes, you might as well invite 32·7 more guests to dinner as use 48 sperm candles to supply the needed illumination.

The flame of acetylene, in spite of its high illuminating value, is a distinctly cool-flame, and in experiments which I have made by means of the Le Chatelier thermo-couple, the highest temperature in any part of the flame is a trace under 1000° C., whilst with coal-gas burning in the same way in a flat-flame burner, the temperature rises as high as 1360° C., whilst if the heating effect of the flames be contrasted for equal illumination, it will be seen that the acetylene flame has so small a heating effect, considering its area, that it would not be much greater than the ordinary electric incandescent lamp.

The intensity of the light will make small acetylene lamps of enormous value for lantern projection, for railway signals, and, coming down to smaller things, bicycle lamps; whilst I should imagine the ease of production specially adapts it for such purposes as lighthouse illumination.

The scope and possibilities of such a discovery as that which I have brought before you this evening cannot be realised until many factors, at present unknown, are thoroughly worked out, and you must remember also that the time at my disposal has only enabled me to bring before you to-night some factors connected with the light-giving value of this hydrocarbon, and that, as a stepping-stone to the synthesis of other bodies, its value will be incalculable; and one cannot help feeling that, as science grows, and as our grasp and comprehension of the marvellous processes by which Nature builds up her matter become more and more extended, synthesis may have even greater conquests to make than the mere building up on a commercial scale of an illuminating hydrocarbon.

We are beginning to realise more and more fully the marvellous way in which Nature keeps matter in circulation, the way in which animal and vegetable structures are built up from the simplest and most plentiful substances, and the way in which, when the structure is done with, those processes of slow combustion which we call decay again convert the waste bodies into carbon dioxide and water vapour, from which once more Nature reconstructs the vegetable and animal kingdon; and it may be that as our perception of the methods of that marvellous natural architecture gets clearer and keener, we may discover how, by simple synthetic processes, the carbon dioxide and water vapour, which form Nature's building material, may be synthetically utilised by us in building up, not the perfected form of man, or animal, or plant, but the building on a commercial scale of the food which is required by Nature for carrying on the functions necessary for life.

ON THE

HYGROSCOPIC CHARACTER OF IODINE AND ON THE DETERMINATION OF ITS MOISTURE.

By C. MEINECKE.

Pure iodine, absolutely dry, spread out flat in a porcelain capsule, but protected from dust, was exposed for a considerable time to the action of the air in the laboratory. From time to time the quantity of water taken up was determined indirectly; the iodine thus exposed being compared volumetrically with pure iodine which had been preserved in air-tight glasses.

The experiments proved that iodine is not changed by the absorption of water in the course of a few hours. Even after five days it had lost very little of its iodometric value. After three weeks the difference reached nearly 0·06 per cent. Hence the attraction of water from the air by iodine is very slightly perceptible.

In a second series of experiments, iodine, recently sublimed, was placed under a bell along with a capsule of water, and compared from time to time with dry iodine.

The experiments showed that even pulverulent iodine can take up only about 0·1 per cent of moisture even under the condition most favourable for attracting water, and which can only be produced artificially. Iodine in leaflets, in well-preserved crystals, can condense on its surface only 0·05 per cent of water. In presence of sulphuric acid moist iodine loses all its water.

Meinecke determined the water in iodine in the following simple manner :—The iodine to be examined he lets fall from a weighing-glass into a dry test-tube of about 1 c.m. in width and 6 c.m. in length, superstratifies it then with at least four or five times the quantity of ignited silver-powder, closes the tube with a glass stopper ground to fit, and weighs either at once, or if the action of the iodine on the silver has been aided by a rise of temperature, complete cooling. The tube is then opened, placed in a small beaker, and heated on an asbestos plate so gently, that the formation of silver iodide takes place very slowly. The temperature can be regulated in case of need by removing the beaker from the plate. With a little experience the process may be so conducted that mere traces of iodine escape. Should such an escape really occur it is at once indicated by the change in the colour of the silver iodide. The silver powder then appears attached to its surface, whilst with correct management the upper layers of the silver should remain unchanged. During the formation of the silver iodide the escaping water is condensed on the colder parts of the tube, from which, after the complete absorption of the iodine, it may be expelled by the application of heat. When this has been effected the tube is stoppered, allowed to cool, and weighed. The difference shows the quantity of water which was present in the iodine. The determination with the preparatory operations requires scarcely an hour.

The author has applied the method both to dry iodine and to such as had been moistened by the addition of small weighed quantities of water.

The author's analysis show that the indirect determination of water is quite accurate. But the method can be combined, either weighing by absorption, by means of a tube ground to fit the desiccation tube, and containing calcium chloride or phosphoric acid, into which the escaping water may be driven by the application of gentle heat.

The method is trustworthy even if the iodine contains chlorine and bromine, but not if cyanogen is present, as cyanogen iodide is then liable to be volatilised.—*Chemiker Zeitung.*

CONTRIBUTIONS TO VOLUMETRIC ANALYSIS.*

By B. REINITZER.

Preparation and Use of Pure Sodium Carbonate as Original Standard for Acidimetry and Alkalimetry.

Among the many substances which have been proposed as original standards for acidimetry and alkalimetry pure sodium carbonate, originally proposed by Gay-Lussac, still remains in almost exclusive use. It is not merely especially suitable from its chemical nature, but meets in an eminent degree the demands to be made upon an original standard.

It is easily obtained in a state of almost chemical purity; it can be weighed without difficulty, and on exposure to a moderate temperature not restricted by any narrow limits it assumes the composition expressed by its formula, so that the chemical effect corresponding to a weighed quantity can be calculated with complete certainty. It has a rather high molecular weight, so that errors in weighing are of the less importance. As the initial material for the preparation of pure sodium carbonate there is used of course sodium hydro-carbonate (bicarbonate), which is met with in commerce in a very pure state, and which is converted into sodium carbonate by a moderate heat not reaching ignition.

If the bicarbonate is contaminated with alkaline chlorides or sulphates it can be easily freed from these impurities by washing with small quantities of distilled water (See Fresenius, "Quantitative Analysis," sixth edition, vol. ii.). At present we find in commerce bicarbonate contaminated with insoluble solids. If we dissolve from 10 to 15 grms. of such a product in hot distilled water there quickly settles to the bottom of the vessel a larger or smaller quantity of a heavy, black, finely-granular powder, which on closer examination is found to consist of iron oxides. Contamination with fine woody fibres is also not uncommon. It will now be shown how from such a bicarbonate contaminated with insoluble matter, and in addition with small quantities of the above mentioned soluble alkaline salts, a perfectly pure sodium carbonate free from insoluble matter may be easily and quickly obtained. About 250 c.c. of distilled water are heated in a tall beaker (preferably of Jena apparatus glass) to 80°, and, whilst constantly stirring, sodium bicarbonate is added in small portions as long as it dissolves at the temperature mentioned. In consequence of the decomposition of the bicarbonate a part of the carbonic acid escapes with so violent effervescence that if the space is insufficient a part of the liquid flows over. However, not one-half, but about one-third, of the total carbonic acid is liberated, yielding ultimately a solution containing 1 mol. sodium hydrocarbonate to 1 mol. sodium carbonate. As soon as further portions of bicarbonate added no longer dissolve, the liquid is filtered into a flask, preferably through a folded filter in a hot-water funnel. The flask is cooled in a jet of water down to 10—15°. An abundance of a coarsely crystalline salt is quickly deposited. This salt is a mixture of bicarbonate with artificial trona, a double salt of the composition—

$$Na_2CO_3+NaHCO_3+2H_2O.$$

It is separated from the mother-liquor (containing along with much trona the small quantities of soluble impurities contained in the bicarbonate) by drainage, suction, and washing with cold distilled water.

In consequence of the coarse crystalline texture of the precipitate the use of a paper filter is quite unnecessary. The glass funnel is closed below with a small Bunsen funnel of strong sheet platinum. Thus we entirely prevent the precipitate being contaminated with paper fibres without danger of its passing through even on the strongest suction. After prolonged drainage the precipitate is repeatedly washed with *small quantities* of *cold* water, which are poured upon the precipitate from a beaker, rapidly and at once, so that the entire mass is kept uniformly moist. According to well-known practice the liquid must be sucked completely off before pouring in a fresh quantity of water.

As the commercial bicarbonate contains only traces of chlorides and sulphates, a few drenchings of water suffice for the production of a perfectly pure salt. The washed salt is now transferred with a platinum or horn spatula to a platinum capsule and heated to a redness scarcely visible by daylight. When cold it is ground up and heated again in the same manner.

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* *Zeitschrift Angewandte Chemie.*

The sodium carbonate thus obtained is quite pure, and even large quantities (20 to 30 grms.) dissolve in water without any trace of turbidity. If we work in beakers of ordinary glass it may occasionally happen that the soda yields a solution not quite clear, but slightly opalescent.

The safest method would be of course to effect the solution of the carbonate in platinum or silver vessels of a sufficient depth. Perhaps nickel vessels, which are now easily procured, might be used with advantage.

In any case we obtain a quite faultless product if we work in beakers of Schott's glass, which resists chemical action much better than ordinary apparatus glass. The yield of pure soda with the proportions above mentioned is 37 per cent of the quantity obtainable by simply heating the bicarbonate employed. If the water used for dissolving the bicarbonate is heated to 100° the yield is smaller, about 22 per cent, and the danger of obtaining a product contaminated with the constituents of the glass is greater.

As pure sodium carbonate slowly attracts water from the air, it should be heated immediately before use. To avoid over-heating and decomposition we proceed as follows:—The powder is placed in a thin-sided porcelain crucible and spread in a thin layer on the sides of the crucible by pressure with a horn spatula. As the powder becomes slightly adhesive by pressure it is easy to produce a uniform thin coating of the sides of the vessel, that is to line the crucible with soda. If we then heat the soda shrinks away from the sides of the crucible and forms a thin-sided soda crucible, the sides of which are pervaded by the heat with uniform rapidity and ease. The heating can of course be effected in a platinum crucible, but we must then be more cautious, lest sintering and fusion of the soda occur, attended with a loss of carbonic acid. This method of heating in a thin layer is also adopted for determinations of moisture in salts much better than the common method in which the expulsion of the water from the interior of the saline mass in the crucible is practicable only if the outside is over-heated.

The salt is then ground up whilst still hot, and filled into a weighing bottle. The quantity of soda required for the primary standard is then approximately measured out of the weighed glass with a horn spoon, and the glass is weighed again. To avoid loss the soda is filled in over a dry funnel inserted into the flask to be used for titration. The horn-spoon is left in the funnel, and both are rinsed into the flask with hot water. Cold water causes the soda to adhere together into a hard lump, which resists the action of the acid for a long time. In hot water the soda remains pulverulent and dissolves quickly. This manner of weighing out and transferring has advantages as compared with the customary method of shaking out of a tube. No powder remains adhering to the neck of the tube which occasions losses or the absorption of moisture, and there is no danger of introducing too much or too little of the soda into the flask. The weighing bottle after being grasped in the hand must be allowed to stand on the scale of the balance for at least fifteen minutes before weighing. If it is weighed immediately after being handled the flask appears 0·5 or 0·7 m.grm. too light. An error in weighing of 0·5 m.grm. causes, however, if we weigh about 2·6 grms. of soda (corresponding to the consumption of about 50 c.c. of normal acid) an error of 0·0003 in the correction figure. By "correction figure" we here signify that number of which the c.c. consumed of a standard liquid not quite correctly adjusted must be multiplied to convert them into normal acid. If, *e.g.*, there have been weighed out 2·70615 grms. Na_2CO_3, this quantity corresponds to—

$$\frac{2{\cdot}70615}{0{\cdot}05338} = 50{\cdot}696 \text{ c.c.}$$

of normal acid, *i.e.*, for its neutralisation there would be required 50·696 c.c. of an accurate normal acid.

If of the acid to be tested there were really consumed for this purpose 50·06 c.c., the correction number of this acid—

$$B - Z = \frac{50{\cdot}696}{50{\cdot}06} = 1{\cdot}0127,$$

i.e., 1000 c.c. of the tested acid for conversion into a normal acid must be made up to 1012·7 c.c., or otherwise every value read off of the acid being tested must be multiplied by this number for conversion into c.c. normal. The soda weighed out is introduced as above described into a flask of Jena apparatus glass containing about 800 c.c. mixed with 300 c.c. of hot water and a few drops of solution of litmus, and so much of the acid to be tested that the liquid appears just of an onion red. It is then heated to ebullition and kept in that condition for eight minutes. Long experience and many special experiments have shown me that at this dilution it may be boiled twice or three times as long without danger of losing even a trace of hydrochloric acid.

This is very important, since normal hydrochloric acid has so many advantages in comparison with sulphuric acid that it should be used exclusively. In addition to the advantages mentioned in Lunge's "Pocket-book for the Alkali Manufacture," it has, like the nitric acid, the highest avidity (tendency to neutralisation) of all acids, and in consequence gives with litmus a much sharper change of colour than sulphuric acid. The solution of constituents of the glass (alkali) during boiling is in case of Jena apparatus-glass so trifling that it has not the slightest influence on the result.

If we do not boil longer than from seven to eight minutes, a time fully sufficient for expelling the carbonic acid, the adjustment in case of normal acids can be effected with full satisfaction in a flask of common glass. The error committed is scarcely measurable with normal acids. Immediately after boiling, the flask, whilst being kept in constant agitation, is held in a stream of cold water, and when thus cooled it is titrated back with alkali. Any good ordinary flask will bear the sudden strong refrigeration if care is taken that the entire surface is overflowed with the cold water. A strong current of water or the total immersion of the flask in cold water is less dangerous than a partial treatment with little water. All fear of breakage is entirely obviated by the use of Jena apparatus-glass.

As long as we work with soda in normal liquids refrigeration is not absolutely necessary. The change of colour is sufficiently sharp in heat. Cooling is indispensable only for decinormal liquids and when titrating with ammonia. The reading off of the volumes of liquid consumed with burettes with fine graduation marks, which for 0·1 c.c. are 1 m.m. distant from each other, can with practice be carried to 0·02 c.c.

The use of an Erdmann float is not only quite superfluous, but on grounds which Mohr has explained it is even objectionable.

(To be continued).

People's Palace Technical Schools.—The annual meeting of the People's Palace Chemical Society will be held on Thursday, January 24, when Professor Thorpe will give an address on "Some Conditions and Causes of Chemical Change." The chair will be taken by Professor Tilden at 8 p.m. Tickets may be obtained on application to the Hon. Sec., Mr. Thomas Yetton.

A Contribution to the Knowledge of the Opium Alkaloids.—O. Hesse.—Laudanidin resembles laudanin very closely in crystalline form, solubility in various menstrua, behaviour with ferric chloride, sulphuric acid, potassa, and soda-lye. It melts in Roth's apparatus at 177° (laudanin at 166°). Codamin is isomeric with laudanin and laudanidin, and homologous with laudanosin. Laudanin probably consists of two bases, the one lævo-rotatory, and the other as strongly dextro-rotatory.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 20th, 1894.

Dr. Armstrong, President, in the Chair.

Messrs. Claude Smith and Frederick J. Allen were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Herbert Anderson, County School, Wellington, Somerset; Francis H. Carr, Meaburne, Warham Road, Croydon; Donald St. John Grant, M.A., M.B., Lahore, India; Herbert Grime, 11, Church Road, Chorlton-cum-Hardy, Manchester; John Adams Hatfield, 89, Bridge Street, Wednesbury; Percy Hudson, 48, Alexandra Road, Burton-on-Trent; Patrick Henry Kirkaldy, 68, East India Road, Poplar, E.; William Baxter McVey, 301, Saratoga Street, Boston, Mass.; Herbert Frederick Stephenson, 10, Muschamp Road, E. Dulwich, S.E.; Thomas C. Warington, 1, Charles Street, Hanley, Staffordshire; Henry Stow Young, 13, Balham Grove, S.W.

The following is the text of an address which has been sent to Professor C. Remigius Fresenius, who has now been fifty years a Foreign Member of the Society:—

"Geh. Hofrath Professor Dr. C. R. Fresenius,

"Dear Sir,

"It is little more than two years ago that the Chemical Society addressed its congratulations to Prof. Bunsen, its senior Foreign Member, on the 50th anniversary of his election into our body. It is now our privilege, on behalf of the Fellows, to address you, who come next to him on our list of Foreign Members, on a similar occasion; and to congratulate you on having so long retained your vigour and pursued your career of usefulness in that most important branch of our science, analytical chemistry, the cultivation of which you have made so especially the work of your life.

"We rejoice to have your name among those of the early contributors to our journal, communications from you on an improved method for the detection and quantitative determination of arsenic, and on inorganic constituents of plants, appearing in the second volume of our Memoirs. Indeed, you were elected into our Society at a time when it was customary to choose as Foreign Members only those chemists abroad who had become directly and intimately connected with us by contributing to our Proceedings, your name coming very early on a list of such contributors at the head of which are the names of Liebig and Bunsen.

"There are still some among us who knew you as a student; not a few also who have been students under you; but you are also well known to the Fellows generally, all of whom, indeed, feel that they owe you much gratitude for the assistance that you have afforded them, both in their studies and in their professional work, through your invaluable text-books on qualitative and quantitative analysis, and through the *Zeitschrift* you have so long conducted, which renders such signal service to chemists by keeping them informed of the progress of analytical chemistry.

"On behalf of English chemists generally, we have to express the earnest wish that you may be permitted during many years to come to continue to carry on labours which are so generally appreciated."

H. E. Armstrong, *President.*
T. E. Thorpe, *Treasurer.*
J. M. Thomson, Wyndham R. Dunstan, *Secretaries.*
R. Meldola, *Foreign Secretary.*

Of the following papers those marked * were read:—

*81. "*An Improved Form of Barometer.*" By J. Norman Collie, Ph.D.

In the improved form of barometer described by the author, several new devices are introduced. Lightness and strength are secured by using for the stem of the instrument thick Sprengel pump tubing. The upper and lower part of the barometer is made from the same piece of tubing, so that the diameter of the cisterns is the same throughout.

Just below the upper cistern a small glass trap is inserted to prevent air which may creep up the stem from entering the Torricellian vacuum. The mercury in the lower cistern is connected with the upper part of the barometer by means of a small tube of capillary bore. This capillary tube is bent just below the point of junction with the bottom of the Sprengel tube, so as to lie along the inner wall of the lower cistern; by this means an unobstructed view of the top of the mercury at the lower level is obtained.

The scale may be etched either on the barometer itself or on a thick plate-glass mirror, which is placed behind the instrument. Very accurate readings are thus obtained.

Mr. C. E. Müller has suggested a further improvement in the form of a ground-glass joint inserted in the middle of the barometer. This renders the instrument easier to fill and clean, besides allowing of its being packed in a box of convenient form.

*82. "*The Constituents of Piper Ovatum.*" By Wyndham R. Dunstan, F.R.S., and Henry Garnett.

This is a West Indian medicinal plant growing in Trinidad. When chewed it gives rise to a tingling sensation and profuse salivation, accompanied by temporary local anæsthesia. The leaves were found to contain a terpene, and a considerable quantity of physiologically active resin, which is also present in the root and stems. From this "resin" the authors were ultimately able, by a tedious process, to separate a crystalline highly active substance, which they name *piperovatine*. Its composition is expressed by the formula $C_{16}H_{21}NO_2$, and it appears to possess an alkaloidal structure, but is, nevertheless, devoid of basic properties. It is nearly insoluble in water and in dilute acid and alkalis, but dissolves readily in alcohol, and the alcoholic solution exhibits the curious property of setting to a "jelly" of very minute crystals when water is added to it.

Piperovatine acts as a temporary depressant of both motor and sensory nerves, and also as a heart poison. It produces a powerful stimulant effect on the spinal cord, causing a tonic spasm resembling that of strychnine. It seems likely to be of service in therapeutics.

*83. "*Note on the Active Constituent of the Pellitory of Medicine.*" By Wyndham R. Dunstan, F.R.S., and Henry Garnett.

The similarity in the physiological effect produced by *Piper Ovatum* and by the Pellitory of medicine (*Anacyclus pyrethrum*), led the authors to examine this plant, the activity of which is usually ascribed to a resin. The authors have separated from this resin a crystalline intensely active substance which they name *pellitorine*. In most of its chemical and physical properties it closely resembles piperovatine; but so far it has always exhibited certain small differences which may possibly disappear when the substance has been further purified. Both piperovatine and pellitorine appear to be pyridine derivatives, but neither possesses any appreciable basic power.

*84. "*The Determination of some High Temperature Freezing-points by means of Platinum-resistance Pyrometers.*" By C. T. Heycock and F. H. Neville.

From time to time the authors have communicated to the Society the results of experiments on the freezing-points of alloys in which sodium, tin, bismuth, cadmium, thallium, and lead were the solvent metals. These experiments have now been extended to temperatures above those in which a mercury thermometer could be used by means of a platinum-resistance pyrometer.

The results, recorded to the nearest whole number, are as follows:—

	Freezing-point.
Zinc	419° C.
Antimony	624 ,,
Magnesium	633 ,,
Aluminium	653 ,,
Silver	957 ,,
Copper	1081 ,,
Sodium carbonate	848 ,,
Sodium sulphate	883 ,,
Potassium sulphate	1066 ,,

In making an experiment the pyrometer is plunged into a mass of the molten substance well above its melting-point, and the falling temperature is followed until it suddenly stops. This temperature is the *freezing-point*. In the apparatus employed the temperature of freezing is maintained for a minute or more, and after this a fall is obtained which at first is very slow. If the pyrometer is now withdrawn it is found to have a very considerable quantity of solid substance adhering to it.

Discussion.

Mr. Gowland called attention to the fact that the metals experimented on were not examined for impurities, although care had been taken to procure them as nearly pure as possible from manufacturers.

Zinc as met with in commerce always contains considerable amounts of lead. In some specimens only 0·4 per cent is present, but in others as much as 1·9 per cent, and even more, is occasionally found. Zinc also contains cadmium, and this is especially the case in the so-called "pure" re-distilled metal. Whilst investigating a method for the determination of antimony in copper by the nature of the fracture of one of its alloys with zinc, he had noticed that ordinary zinc (spelter) gave satisfactory results, but when so-called "pure" zinc which had been re-distilled by the manufacturer was used, the results were altogether anomalous. On examining this zinc it was found to be contaminated with cadmium, two cakes containing 5·1 per cent, another about 3 per cent, and a fourth little more than traces.

In the case of copper, commercial samples vary much in the proportions of metallic impurities and of sub-oxide present. Even electrotype copper is sometimes impure; copper should therefore always be tested, the simplest method being a determination of its electric conductivity, as this will generally sufficiently indicate the extent of its purity. Copper when melted, even under a thick layer of charcoal, will absorb oxygen, and become contaminated with sub-oxide.

He suggested that it would be desirable in future to ascertain the chief impurities in the metals experimented on, and to determine their amounts, for even when present in small proportions they often have, as is well known, marked effects on the physical properties. This would add very greatly to the value of the determinations of their freezing-points, and would enable them to be compared with the results obtained by other observers.

*85. "*The Preparation of Adipic Acid and some of its Derivatives.*" By Walter H. Ince, Ph.D.

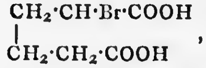
Wislicenus's method of preparing adipic acid by heating β-iodopropionic acid with silver being found to be unsatisfactory, other methods of preparation were investigated.

According to Arppe (*Zeitsch. fur Chem.*, 1865, 300), adipic acid may be readily prepared by the action of nitric acid on sebacic acid. The author finds, however, that not only has nitric acid no action on sebacic acid, but that sebacic acid crystallises unchanged from its solution in fuming nitric acid. By the action of potassium permanganate in neutral acid, and alkaline solutions, sebacic acid is entirely decomposed, yielding small quantities of a monobasic acid, but no adipic acid.

Malaguti (*Ann. Chim. Phys.*, [3], xvi., 84) states that when beef suet is heated with ordinary nitric acid, the main product is adipic acid. The author in repeating the experiment finds that when ordinary nitric acid is used, the main product consists of sebacic and azelaïc acids, and, when fuming nitric acid is used, an acid having the formula $C_{11}H_{20}O_4$ is among the products. In neither case could the presence of adipic acid be detected.

As might be anticipated, the action of nitric acid on beef suet is a complex one, and the products vary with the concentration of the acid employed; but in no case does adipic acid appear to be formed.

α-Monobromadipic acid,—



$$\begin{array}{l}CH_2{\cdot}CH{\cdot}Br{\cdot}COOH\\ |\\ CH_2{\cdot}CH_2{\cdot}COOH\end{array},$$

was prepared by Gal and Gay-Lussac (*Annalen*, clv., 250), but was not obtained in a pure state. The author has isolated it in a state of purity by heating adipic acid (1 mol. prop.) with bromine (2 mol. props.) in a sealed tube at 160° for two hours. The semi-crystalline contents of the tube are dissolved in ether, and yield on re-crystallisation from absolute alcohol, small colourless crystals melting at 131°. When mixed with water or a dilute solution of potassium hydroxide, this acid readily changes into *α-hydroxyadipic acid*, $C_4H_7OH(COOH)_2$. This is extracted from the aqueous solution by ether, which on evaporation deposits colourless crystals melting at 151°, and subliming without decomposition. This acid is soluble in alcohol, water, and ether.

*86. "*The Action of Hydrogen Chloride on the Oxides of Calcium, Barium, and Magnesium.*" By V. H. Veley, F.R.S.

In continuation of former experiments (*Trans.*, 1893 and 1894), the author finds that dry hydrogen chloride does not act on quicklime at ordinary temperatures, or at 40°, but at 80° action occurs. Dry hydrogen chloride does not act on magnesia at ordinary temperatures; at 40°, however, action takes place to a considerable extent. Dry hydrogen chloride was observed to attack baryta at all temperatures.

Discussion.

The President expressed the opinion that our knowledge of the conditions which determine chemical change, and of the influence of water, was now such that it was necessary to adopt every possible precaution in preparing dry materials, and that the mere passage of a gas *over* a drying agent was not sufficient. He thought that on this account Mr. Veley's results were entirely inconclusive, and that the enquiry ought to have been carried further before an attempt was made to state conclusions. It was to be expected that barium oxide would be more easily acted on, as baryta was dehydrated less readily than lime or magnesia.

* 87. "*Latent Heat of Fusion.*" By Holland Crompton.

If the latent heat of fusion of a unit weight of a metal is multiplied by the atomic weight of the element and divided by the absolute temperature of fusion, the resulting quantity is proportional to the valency of the metal, or in other words equivalent quantities of the metallic elements undergo on fusion equal changes in entropy. In modified form this rule is found to hold also for the non-metals.

In the case of compounds the molecular latent heat of fusion divided by the absolute temperature of fusion is also proportional to the sum of the valencies of the atoms composing the molecule. It is necessary, however, in this case to suppose that the valencies are to a certain extent influenced by the mode of union of the atoms with one another, and modified in accordance with certain definite empirical rules stated by the author.

For elements, therefore, the relationship $wA/Tv = 1{\cdot}38$, and for compounds the similar relationship $wM/T\Sigma v = 1{\cdot}38$ is found to hold: w is the latent heat of unit weight, A the atomic and M the molecular weight, T is the absolute temperature of fusion, and v and Σv are the valencies and the sum of the valencies respectively.

By combining these expressions with van 't Hoff's formular for the molecular depression of the fusing point, $E=0{\cdot}02T^2/w$, it is possible to calculate the molecular depression from the values of v and T. The numbers thus calculated are compared with those obtained by direct measurement and found to be in fair agreement. Solubilities or the melting points of mixtures of known composition can also be calculated, making use of the formula given by Schröder (*Zeit. Physikal. Chem.*, xi., 449), connecting the solubility with the latent heat of fusion and melting-point in absolute temperature. Here, again, agreement between the calculated and observed values is obtained.

The relationship enunciated in the paper throws a new light on the question of the mechanism of the change from the solid to the liquid condition. It indicates that this change is one in which the simple chemical molecules and the atoms composing them are mainly concerned, and that it does not consist merely in the transition of complicated to simpler molecular aggregates.

88. "*Metallic Tartrarsenites.*" By G. G. Henderson, D.Sc., M.A., and A. R. Ewing, Ph.D.

Arsenious oxide dissolves readily in hot solutions of sodium hydrogen tartrate, and when the liquid is concentrated and cooled, colourless prismatic crystals of *sodium tartrarsenite*, $C_4H_4O_6AsONa{\cdot}2\frac{1}{2}H_2O$, separate. This is a stable salt, easily soluble in water, but insoluble in alcohol. The aqueous solution has an acid reaction, and when neutralised with soda gives a mixture of arsenious oxide and disodium tartrate. The corresponding *ammonium* salt resembles the sodium salt, but is more unstable, gradually decomposing, even in the solid state, into arsenious oxide and ammonium hydrogen tartrate. *Potassium tartrarsenite* is at once decomposed by cold water, and hence is prepared with greater difficulty. It is obtained as a finely crystalline precipitate. The characteristic *barium* salt, $(C_4H_4O_6AsO)_2Ba{\cdot}H_2O$, is prepared in the form of delicate lustrous needles by mixing dilute solutions of barium chloride and of the sodium salt. It is only slightly soluble in hot water, and is partially decomposed when boiled with much water, like all the salts of the series hitherto examined. The *strontium* and *calcium* salts are more soluble, and much less stable in solution. The heavy metals give precipitates with soluble tartrarsenites, but these precipitates appear to be in most cases either tartrates or mixtures of tartrates with arsenious oxide.

When the barium salt is cautiously mixed with dilute sulphuric acid, keeping the salt in excess, a clear filtrate is obtained, which has a strong acid reaction, but contains no sulphuric acid, and which gives a copious precipitate of arsenious sulphide when hydrogen sulphide is added. The solution probably contains free tartrarsenious acid, $C_4H_4O_6AsOH$, but this is too unstable to be isolated. Concentration of the solution, or raising its temperature to 60—70°, or addition of alcohol or of a trace of a mineral acid, causes decomposition of the acid into arsenious oxide and tartaric acid; but if soda is added, sodium tartrarsenite is formed, and a quantitative examination of the solution proved it to contain almost exactly the theoretical quantity of arsenic.

Experiments with other acid oxides and hydoxy-acids indicate that tartrarsenious acid is either a derivative of arsenious acid,—

$$As\begin{matrix} \diagup C_4H_4O_6 \\ \diagdown OH \end{matrix},$$

or an ethereal derivative of tartaric acid, having the formula $CO_2H{\cdot}CHO(AsO){\cdot}CHOH{\cdot}CO_2H$.

89. "*Note on the Interaction of Hydrogen Sulphide and Bismuth Haloid Compounds.*" By M. M. Pattison Muir, M.A., and Edwin M. Eagles, B.A.

The authors find that bismuth chloride and hydrogen sulphide react at a very moderate temperature, producing bismuth thiochloride, BiSCl, and hydrogen chloride; that a similar action occurs between bismuth bromide and hydrogen sulphide; but that bismuth iodide and hydrogen sulphide do not interact. They also prove that bismuth sulphide is produced by the interaction of bismuth chloride, or bromide and hydrogen sulphide at a red heat. The thiohaloid compounds, BiSCl and BiSBr, are also formed very readily by passing chlorine or bromine vapour over bismuth sulphide. Bismuth thioiodide was obtained, but not quite free from bismuth sulphide, by heating bismuth sulphide with bismuth iodide.

PHYSICAL SOCIETY.

Extra Meeting, January 11th, 1895.

Prof. A. W. Rücker, F.R.S., President, in the Chair.

This meeting was held in the physical laboratories of University College (by invitation of Professor Carey Foster).

Prof. Ramsay read a paper by himself and Miss Dorothy Marshall on "*The Measurement of Latent Heats of Vapourisation of certain Organic Liquids.*"

The liquid to be examined is placed in a small flask with a narrow neck, and within this is a platinum wire which has its two ends fused through the bottom, so as to be capable of conveying an electric current and thus giving heat to the liquid. The flask is completely enclosed in a jacket which is filled with the vapour of liquid of the same kind, kept briskly boiling in a somewhat larger flask. Before the current is turned on the vapour jacket is kept going for some time, so that the liquid in the flask is raised just to its boiling point, but no appreciable evaporation takes place. As soon as the current is turned on, boiling commences, and as the temperature of the liquid cannot be further raised, all the heat developed in the wire is expended in producing evaporation. By weighing the flask before and after, the mass of liquid vapourised is determined. So far the authors have only used the method for comparative determinations. Two arrangements of the kind described are placed side by side, and the same current is sent through their two wires, which are joined in series and have approximately equal resistances. The actual values of the resistances are found while the current is flowing, and allowance is made for their inequality. The ratio of amounts of heat expended on the two liquids divided by the ratio of the masses vapourised, is equal to the ratio of their latent heats. As a standard liquid of known latent heat, the authors prefer alcohol to water, as it vapourises more easily and with less bumping. The determinations made by this method agree well with those of other observers, but the authors' object is to obtain values correct within about $\frac{1}{2}$ per cent for a large number of liquids rather than a highly accurate value for any one substance.

In reply to Mr. Griffiths, the authors stated that the platinum wire was found to rise about 20° above the temperature of the liquid, and Mr. Griffiths said that his experience had been similar. He did not see why a very high degree of accuracy should not be obtainable by the method.

Prof. Rücker expressed his admiration for the work, and thought it justified by the fact that the results accorded more nearly with theory than those of other observers.

Mr. Eumorfopoulos read a paper on "*The Determination of Thermal Conductivity and Emissivity.*"

In the first series of experiments described, two bars of the same material and polish, and each of the uniform circular section, are heated, each at one end, until the distribution of temperature has become steady. By means of two thermo-joints (one on each rod) a series of isothermal points are then found. According to the ordinary theory, if the two bars agree in temperature at a given pair of points, they will also agree in temperature at distances x_1 and x_2 measured respectively from these points, where x_1 and x_2 are connected by the relation $x_1/x_2 = \sqrt{(r_1/r_2)}$; r_1 and r_2 being the radii of the rods. This relation was not found to hold good for the rods examined, some being of brass, others of copper and of German silver. In all cases x_1/x_2 was further removed from unity than the ordinary theory would require. One conclusion was that the formula usually adopted in such cases could not be used for the comparison of conductivities, unless the radii of the rods compared are equal, and their surfaces in the same condition. For it seemed unlikely that the thermal conductivity of the smaller of each pair of rods was less than that of the thicker one. To settle the question, three brass rods were chosen, and their absolute conductivities compared by Angström's method, one end of the rod being alternately heated and cooled, and the alternations of temperature observed at two points along the rod, as soon as they had assumed a periodic character. At each point of the bar the excess of temperature over surroundings may be analysed into a Fourier's series, consisting of a constant term and series of sines and cosines. Hence both emissivity and conductivity were calculated. The emissivity was found to vary considerably with the radius, being greater the thinner the rod; moreover the value of the emissivity deduced from the first sine term of the Fourier's series was in each case found to be about 1·2 times as great as that deduced from the constant term.

Mr. A. W. Porter then read a paper "*On the Influence of the Dimensions of a Body on the Thermal Emission from its Surface.*"

The ordinary assumption is that whether a body is *in vacuo* or surrounded by air, the "emissivity" (*i.e.*, the amount of heat passing outward from unit area per second per degree excess of temperature) is independent of the size of the body. Results obtained experimentally by Péclet for cylinders and spheres of different sizes show that the emissivity depends materially upon the size of the body. Péclet's formulæ for cylinders and spheres surrounded by air show that for each of these forms the rate of emission per unit surface, exclusive of the radiation effect, may be represented by a constant *plus* a term inversely proportional to the radius. Experiments on thin wires by Messrs. Ayrton and Kilgour have also shown that the emissivity can be expressed through a considerable range of radius in the form given by Péclet, and the experiments on rods made by Mr. Eumorfopoulos and already described in this report lead to the same conclusion. The author examines the results of supposing the loss to follow only in part the law of radiation, the remainder being assumed to follow the law of conduction. He thus arrives at a formula—

$$e = h + \frac{c}{a\,(\log \mathrm{R} - \log a)},$$

where e is the emissivity, a the radius of the rod, R the radius of a hollow cylinder which surrounds the bar, and above which the excesses of temperature are reckoned, while h and c are constants. This formula has been compared with experimental results of Ayrton and Kilgour, of MacFarlane, of Bottomley, and of Péclet, and has also been directly checked by experiments on a brass rod when surrounded by water-jackets of different radii, as well as on the same bar unjacketed. The author finds the agreement to be much closer than is the case on the theory of constant emissivity, or with empirically deduced formula of Ayrton and Kilgour; and he concludes that the enclosing boundary is as important a factor in determining emissivity as the size of the body itself.

Prof. Carey Foster thought that in demonstrating the influence of the enclosure Mr. Porter had established an important point.

Prof. Ayrton agreed as to the importance of the influence of the enclosure. Some years ago he had noticed that when the diameter of a wire was small, the power required to keep it red-hot by the passage of a current was nearly independent of the diameter. This would also follow from Péclet's formula. He urged that in such experiments as those of Mr. Porter and Mr. Eumorfopoulos, the conductivity and emissivity, which were functions of the temperature, should not be assumed constant along the bar.

Mr. Trotter objected to the use of the term emissivity as including loss of heat by contact with the air, in addition to the loss by radiation.

Mr. Griffiths said that in some of his experiments, where a wire conveying an electric current was immersed in a liquid in order to heat the latter, the rise of the temperature of the wire above that of the liquid was found to be nearly independent of the diameter of the wire.

Mr. Eumorfopoulos, replying to Prof. Ayrton's criticism, said that in each case his comparison had been between portions of bars in which the range of temperature was the same. Moreover, the variation of the emissivity and conductivity with temperature, as found by other observers, would be quite insufficient to account for his results.

Mr. Porter said that the term emissivity had come to be accepted as referring to all heat lost at the surface of a body, whether by radiation or by conduction and convection. In that sense he had used the term.

Prof. Rücker thought that emissivity, in this sense, was not a good term, but to change now would probably only make greater confusion.

Mr. G. U. Yule then gave a brief outline of his paper "*On the Passage of an Oscillator Wave-train through a Plate of Conducting Dielectric.*"

By a conducting dielectric the author means a substance whose conductivity and dielectric capacity are both of importance in the case under discussion, and the paper is mainly an investigation of the following problem:—A train of plane electromagnetic waves falls at normal incidence on an infinite parallel-sided plate of conducting dielectric, whose thickness is finite, and at the first face of the plate the amplitude of the vibration-vector in the incident train is zero up to a certain instant, and then becomes equal to an harmonic function of the time, multiplied by an exponential function with negative index. To find what proportion of the energy of the whole incident train is reflected back, what proportion is transmitted through the plate, and what proportion absorbed at successive incidences of reflected and re-reflected wave-trains upon the two bounding faces of the plate, the amplitudes and phase-changes of reflected and transmitted portions have to be taken into account, and the resulting infinite series of terms have to be summed. The analysis is very long, but the results obtained are exact. Curves are given showing (for special numerical values of the constants of the problem) the quasi-periodic variation of the amounts of energy transmitted and reflected, as the thickness of the plate is increased from zero up to a high value. Other curves are given showing the effect of varying the dielectric constant and the conductivity of the plate, and the difference between a "damped" and an "undamped" wave-train in regard to intensity of reflected and transmitted portions. The author compares his calculated results with measurements obtained in the case of oscillator-waves travelling along a double-wire circuit about 100 metres in length; the wires at the middle of the circuit being run through a jar containing distilled water, alcohol, or a very dilute electrolyte. The necessary corrections, however, are difficult and uncertain, and the author has not found it possible to deal with them in a satisfactory way.

A letter from Dr. E. H. Barton was read emphasizing the necessity of taking into account the damping in the oscillator-train, and at the same time pointing out why, in his opinion, the corrections applied by Mr. Yule were inadequate and failed to yield intelligible results.

Prof. Rücker congratulated Mr. Yule on his work, and on the importance of the results he had obtained.

In returning the thanks of the Society to Prof. Carey Foster for the invitation to meet in University College, he expressed the pleasure he had felt in observing the extent and completeness of the laboratories. Hitherto London had been behind the provinces in this matter, and it was gratifying to find that students in London had now such opportunities for practical instruction in physics. The papers which had been read at that meeting were a proof that good use was being made of the laboratories for the purpose of research. The educational experiments they had seen in the laboratories were excellently devised, and he hoped that many of them would become a part of the regular course of instruction in the country.

Prof. Foster briefly replied.

NOTICES OF BOOKS.

Outlines of Mathematical Chemistry. The Energetics of Chemical Phenomena. ("Grundzüge der Mathematischen Chemie. Energetik der Chemischen Erscheinungen"). By Dr. Georg Helm, Ordent Professor at the Royal Chemical High School of Dresden. With 17 Figures. Leipzig: Engelmann. 1894.

According to the author's preface, the title of this book must be understood in the same sense in which we speak of mathematical physics. He aims at collating the results of the most recent researches in the field of general chemistry according to the deductive method. Experiments are here, not as in the inductive presentation, to lead to the development of conceptions, but only to illustrate these conceptions and make the reader acquainted with their use. It would almost seem that chemistry is to lose its character as a science of observation and experiment, and in consequence to fall under the jurisdiction of a different class of minds. We cannot say that this revolution is free from a dark side. The new development will require exceptional care and judgment if it is to be truly and permanently useful to Science. It need scarcely be said that to anyone not familiar with the higher mathematics the work is utterly unintelligible.

In the successive parts Dr. Helm discusses energy, entropy, chemical intensity, and, in conclusion, the stage of multiplicity, or the freedom of chemical phenomena. Perhaps he would have done more service had he at the outset or at the conclusion presented his views free from mathematical scaffolding.

Constitution of the Aromatic Sulphones.—L. Zorn and H. Brunel.—From the existence of the paraxylene and orthoxylene sulphones, and from the fact that the sulphones of metaxylene have not been obtained, we believe we may conclude that in the aromatic sulphones the group SO_2 must be placed in the *meta*-position.—*Comptes Rendus*, cxix., No. 26.

Series of Indophenols. General Method of Preparation.—H. P. Bayrac.—The author has used a modification of the method of Kœchlin and Witt. The principle of this method consists in causing paramidodimethylaniline to react upon the phenol, not in an alkaline, but in an acetic solution. The quantity taken of the phenol which it is intended to convert into indophenol is equal to one-fifth of the molecular weight of the phenol. All these indophenols possess a number of physical characters in common. Their crystals, when measurable, belong to the triclinic system. They are almost insoluble in water, which, however, they colour a very fine blue. With ether they give a violet solution; with benzene a violet blue; with alcohol a very fine blue; with ligroine a violet red; with acetic acid a greenish blue. The mineral acids, especially if concentrated and slightly heated, destroy these compounds.—*Bulletin de la Soc. Chim. de Paris*, xi.-xii., No. 23.

CORRESPONDENCE.

THE "PROCEEDINGS OF THE CHEMICAL SOCIETY."

To the Editor of the Chemical News.

Sir,—The title-page and index of this periodical have just come to hand; and on the title-page occur the words—"Edited by the Secretaries." It is right that authors should know the precise significance of these words as lately determined by the Council of the Society.

Two courses appeared to be open:—Either to submit proofs to the authors of the abstracts of their papers sent to the Society if any substantial (*i.e.*, more than typographical) alteration had been made; in which case, the authors themselves would naturally bear the responsibility of their statements. Or, on the other hand, to throw the whole responsibility on the editors, leaving them them to make any excisions or alterations they may choose in the abstracts sent to them; or, indeed, if they so think fit, entirely to re-write them. The Council, in order to secure rapid publication, have chosen the latter alternative; and it should be understood that the abstracts are now "official," *i.e.*, the responsibility for all statements put forth rests solely on the editors of the *Proceedings*.—I am, &c.,

William Ramsay.

University College, London,
January 14, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 26, December 24, 1894.

Displacement of Carbon by Boron and Silicon in Melted Cast-iron.—Henri Moissan.—Already inserted.

L. Joué and E. Crouzel addressed to the Academy a paper on a tanno cupric liquor applicable to the treatment of mildewed vines.

Experimental Researches on Radiation at Low Temperatures.—Raoul Pictet.—The author expresses his results by means of six curves.

Contribution to the Study of Atmospheric Ozone.—J. Peyron.—The author studies the influence of vegetation on the formation of atmospheric ozone. He has made more than seven hundred observations during the months of 1894, July to October inclusive, using the iodised starch ozonoscopic paper. He concludes that vegetation favours the formation of atmospheric ozone. His papers were blackened, and he observes that the papers were least attacked if placed in conditions where oxygen is destroyed, *e.g.*, near putrescent organic matter. In the country he observed ozone every day and every night, but not in Paris except on stormy days.

On the Metallic Sulphides.—A. Villiers.—This paper will be inserted in full.

Combinations of Hexamethyleneamine with Silver Nitrate, Chloride, and Carbonate.—M. Delepine.—The author gives the percentage compositions, the formulæ, and the reactions of these compounds. He points out as remarkable the formation of compounds of silver carbonate and chloride with a base approximating to the amines.

On the Iron Chromates.—Charles Lepierre.—The author has obtained thirteen chromates, two of which only were previously known. There are double salts, and all are ferric. They are in general hydrated. All are coloured from red to yellow, passing through brown tones. The chromates derived from ferrous salts are less rich in chrome than those derived from ferric salts, and among the latter those obtained from the dichromates are the richest. The proportion of iron oxide is greatest in the chromates of the ferrous salts, and it oscillates between 23 and 26 per cent in the chromates of the ferric salts. The iron chromates form a series parallel to the basic sulphates of the same metal. They are applicable in painting on porcelain.

On the Cyanic Ethers.—Albert Colson.—Urethane is a constant product of the reaction of cyanogen chloride with ether. The author has also obtained the soluble and the insoluble cyanic ether. These two compounds are physical isomers. Both are very stable.

New Reagent for showing the Presence of Hydrogen Peroxide in Green Plants.—A. Bach.—The author places in a test-glass 5 c.c. of a solution containing 0·03 grm. potassium bichromate and 5 drops of aniline per litre. He adds 5 c.c. of the solution in question and one drop of a 5 per cent solution of oxalic acid. In presence of hydrogen peroxide there is produced a rose-violet colour. A blank experiment should be made simultaneously. Of the twenty-five plants tried, eighteen gave a positive result. Negative results were obtained with *Medicago sativa*, *Chicorium intybus*, *Avena sativa*, *Viola odorata*, and *Lilium bulbiferum*. These experiments tend to prove that the green parts of plants contain hydrogen peroxide, or peroxides which have a similar function.

On the Valence of Glucinium and the Formula of Glucina.—Alph. Combes.—According to the author's experiments, we ought, as does Mendeleeff, to consider glucinium as bivalent, having the atomic weight 9. The formula of glucina will be $\mathrm{Gl.O}$.

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.

Potassium Cyanide.—The firm of Messrs. Philip Harris and Co, Limited, Birmingham, are manufacturers of potassium cyanide, 100 per cent, at a price of 3s. 9d. per pound.

Restoring Engravings.—I find a number of coloured prints, left in a book for years, have become so affected by some deleterious substance in the paper that the pigment, presumably red lead, has turned almost black with a metallic lustre. Under these circumstances I would ask if there is any acid, alkali, or other chemical with which these works might be treated so as to secure rubification and return to some of their pristine freshness?—Collector.

MEETINGS FOR THE WEEK.

Monday, 21st.—Society of Arts, 8. (Cantor Lectures). "The Arc Light," by Prof. Silvanus P. Thompson, F.R.S.
— Medical, 8.30.
Tuesday, 22nd.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
— Society of Arts, 4.30. "Russian Armenia and the Prospects for British Trade," by Dr. A. Markoff.
Wednesday, 23rd.—Society of Arts, 8. "Tea," by A. G. Stanton.
— Geological, 8.
Thursday, 24th.—Royal, 4 30.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Four English Humourists of the Nineteenth Century," by W. S. Lilly, M.A.
Friday, 25th.—Royal Institution, 9. "The Nile," by Sir Colin Scott-Moncrieff, K.C.M.G.
— Physical, 5. "On Tests of Glow Lamps," by Prof. Ayrton and Mr. Medley. "On the Temperature of Water at its Maximum Density," by Professor Anderson and Mr. McClelland.
Saturday, 19th.—Royal Institution, 3. "Stained Glass Windows and Painted Glass," by Lewis F. Day.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1835.

NATURAL GROUPS AND CROSS-ANALOGIES.

By C. T. BLANSHARD, M.A.

Natural groups of the elements are determined principally by two characters: (1) A simple connection between the atomic weights; (2) the possession of similar chemical properties. These two characters do not always suffice to group elements correctly, owing to the existence of *cross-analogies*, which will be dealt with shortly. A check on these two classifying characters is found, however, in the *dicta* of the periodic law.

Thus, the older chemists would place Cr in the same group with Mn, C in the same as B, and so on.

A list of the elements arranged in their natural groups according to the latest physical and chemical evidences, checked in this way by the periodic law, will be found in the Chem. News (lxx.. p. 271) and in the *Phil. Mag.* ([5], 39, p. 106, January, 1895), in which articles the classification of the elements is examined into from the points of view of *atomic volume*, *atomic heat*, *melting-point*, and *volume heat*.

But, for the purpose of studying various cross-analogies, I will here reproduce this classification, numbering the elements in their groups, as position in a natural group will be found to have an important bearing on the subject.

	I.	II.	III.	IV.
1.	Li	Be	B	C
2.	Na	Mg	Al	Si
3.	K	Ca	Sc	Ti
4.	Rb	Sr	Y	Zr
5.	Cs	Ba	La	Ce
6.	—	—	—	Th

	V.	VI.	VII.
1.	N	O	F
2.	P	S	Cl
3.	As	Se	Br
4.	Sb	Te	I
5.	Bi	Bo?	—

	I.*a*.	III.*a*.
1.	Cu	Ga
2.	Ag	In
3.	Au	Tl

	V.*a*.	VI.*a*.	VII.*a*.
1.	V	Cr	Mn
2.	Nb	Mo	—
3.	Nd?	Pr?	—
4.	—	U	—

	II.*a*.	IV.*a*.
1.	Zn	Ge
2.	Cd	Sn
3.	Hg	Pb

	II.*b*.	IV.*b*.	VI.*b*.
1.	Fe	Co	Ni
2.	Ru	Rh	Pd
3.	Os	Ir	Pt

	I.*c*.	III.*c*.	V.*c*.	VII.*c*.
1.	Sm?	Gd?	—	—
2.	Dp?	—	Ta	—

	II.*c*.	IV.*c*.	VI.*c*.
1.	—	Tb?	Er
2.	Yb	—	W

The *c* groups here are the 10th and 11th periodic series of W. Preyer ("Das Genetische System der Chemischen Elemente," Berlin, 1893).

If we examine into these groups, either regarding the chemical or physical characters of the elements placed in them, we find that several elements might easily be considered as members of different groups than here represented; but that, looked at from the point of view of the majority of their properties, they are correctly grouped, notwithstanding.

Thus, Mendeléeff places Na as the first member of the Cu series ("Osnovoui Chimii," 1873), in which he is followed by Preyer and others; Lothar Meyer ("Moderne Theorien der Chemie," 1891) places it between Li and K. Both classifications have something to be said in their favour. Thus, J. W. Retgers (*Zeit. Phys. Chem.*, iv., 593) finds that sodium and silver nitrates are isodimorphous, viz., that from mixed solutions of the two salts, when $AgNO_3$ is in excess, rhombic crystals form; whilst, when $NaNO_3$ is in excess, hexagonal crystals take their place. Again, until a sodium-alum was produced, exactly like potassium-alums, there seemed good reason to regard Na as deviating considerably from the characters of the K series. E. Augé, however (*Comptes Rendus*, 1890, cx., 1139), by taking care to keep the solutions of the sulphates within certain limits of both t° and concentration, has succeeded in forming a definite Na alum exactly analogous to K alums.

Again, take the first elements of each group, Li, Be, B, C, N, O, and F. Mendeléeff calls these "typical elements," W. Ostwald ("Outlines of General Chemistry," Eng. trans., 1891, p. 185) shows that this name is rather unfortunate; for these elements are rather the connecting links between the various natural groups. Now, this is what we should expect on the hypothesis that the elements have a common origin. The top members of each group would have many characters in common, whereas the lower members of any one group would differ considerably, being specialised in a particular direction from the corresponding lower members of other groups. Thus, Ostwald gives as examples:—Li forms a sparingly soluble bicarbonate, like the metals of the alkaline earths, not like Na and K. Again, Be is so like Al—its oxide resembles Al_2O_3 very closely, its salts are astringent like those of Al, &c.—that, until the atomic heat of the element and the vapour-density of its chloride proved it to be allied to Mg, it was regarded as a triad. The triad Boron resembles no other element so much as it does the tetrad Carbon. The following analogies of fluorine to the first member of the hexad-group, oxygen, have been found by H. Moissan (*Bull. Soc. Chim.*, [3], v., 880):—(1) Charcoal burns in it; (2) calcium fluoride resembles the oxide rather than the chloride; (3) fluorides of metals have higher melting-points than the corresponding chlorides.

Let us take a few more examples, in order to find out the circumstances under which cross-analogies can exist between elements. Mn is isomorphous with Cr in the manganates and chromates, besides several well-known analogies of the two substances in the laboratory. These elements are the first members of two adjoining natural groups.

In the permanganates Mn is analogous to Cl—the permanganates and perchlorates being isomorphous.

Mn and Cr have nearly the same atomic weight. But not only have elements with nearly the same atomic weight cross-analogies, but also elements of nearly double (or nearly half) the atomic weights of others are analogous. Thus,—

$$\text{Cr} = 52 \text{ and Al} = \frac{54}{2}$$

are isomorphous in the alums.

A similar analogy was instanced by the writer as early as 1875 (Chem. News, xxxii., 151). Hg, with atomic weight 2×100, is analogous in its protosalts to Ag=108. This subject is being worked at by J. Traube (*Berichte*, No. 18), an account of which is given in the Chemical News (vol. lxx., p. 314).

Cu, besides being isomorphous with Ag, with which it is grouped by the periodic law, is, in certain compounds, isomorphous with Fe, Co, and Ni. These four elements have very similar atomic weights, but their atomic volumes are still closer, being nearly identical, viz., about 7. The same fact is observed in Cr and Mn, with atomic volume 7·4, and in numerous other cases of isomorphism. The connection between isomorphism and atomic volume was discovered by Schröder in 1865.

Cr has analogies with both Co and Rh (IV.*b*, 1 and 2). S. M. Jörgensen (*Journ. Prakt. Chem.*, [2], xli., 437) has investigated some complex bases containing ammonia and chlorine combined with Cr, Rh, or Co, of analogous composition.

Again, with regard to Al, P. Hautefeuille and A. Perrey (*Comptes Rendus*, cvii., 786) have found that Be can replace Al (1) in silicates of the composition—

$$6SiO_2,R_2O_3,K_2O\,;$$

(2) in orthoclase. Al, on the other hand, has analogies to Cr and Fe in the alums; whereas Fe as a dyad is isomorphous with dyad Zn and Mg.

In some salts Ca is isomorphous with Zn and Mg, in others with Pb, as are also Ba and Sr.

The hexad elements Mo and W are found by J. W. Retgers (*Zeit. Phys. Chem.*, viii., 6—75) to be analogous to heptad Mn by the isomorphism of K_2MoO_4, K_2WO_4, and K_2MnO_4.

W. Feit has shown ("Dissertation," Lippstadt, 1888) that Tl, though connected with the Al, Ga, and In group by its atomic weight, atomic volume, &c., has the following analogies to members of other groups:—*a*. To Pb in having nearly the same atomic volume, and in the fact that a thin layer of carbonate forms on it in the air. *b*. Thallium resembles K even more closely than it does Pb; thus (1) the carbonate is soluble in water; (2) the chloride forms double salts with $PtCl_4$; (3) its tri-iodide is like KI_3; (4) according to C. Lepierre and M. Lachaud (*Comptes Rendus*, cxiii., 196), it forms with potassium chromate the crystalline double salt $KTlCrO_4$, but not with lead chromate. To this we might add (5) the simple spectra of K and Tl, that of Pb being very complex.

Tl and Pb are the third members of groups III.*a* and IV.*a*, K being the third member of group I., and we have seen they have several analogies. In the same way the last members of groups IV. and VI.*a*, Th and U, show analogies, though to a less extent.

Thus, W. F. Hillebrand and W. H. Melville (*Amer. Chem. Journ.*, xiv., 1) find that their sulphates are isomorphous.

I think enough evidence has been cited to show that elements occupying corresponding positions in natural groups, especially in adjoining groups, offer many analogies (law of cross-analogies).

THE NOMENCLATURE OF THE PENTOSES AND PENTOSANS.

By W. E. STONE.

There has just come to my notice the suggestion of C. F. Cross in the Chemical News for December 21st as to the nomenclature of the "furfural yielding carbohydrates." It hardly seems possible that the writer is unacquainted with the terms "pentoses" and "pentosans" already in common use to designate these very bodies, although he makes no reference to them.

The furfural reaction as applied to carbohydrates is given only by the pentatomic sugars or by certain amorphous substances, which upon hydrolysis yield one or the other of these sugars. The sugars are properly named "pentoses," expressing their position in the homologous series of aldoses, including the "hexoses," "heptose," &c. All of the amorphous bodies which yield furfural in appreciable quantities under the standard conditions (distillation with dilute mineral acids) yield, when hydrolysed, in every case thus far studied, one or the other of the pentoses. The name "pentan" was applied by me to such bodies in a paper in the *American Chemical Journal*, xiii., No. 5, and also published in the *Berichte*, xxiv., p. 1657. Soon after, at the suggestion of Professor Tollens, and to avoid confusion with the term "pentane" as applied to the hydrocarbon C_5H_{12}, the name "pentosan" was first used by me in a paper in the *Journal of Analytical and Applied Chemistry*, v., No. 8. Since then the term has come into general use by writers upon this class of bodies. It expresses the relation of such bodies to the pentoses, which seems of more importance than to indicate that they both undergo a similar reaction. A use of analogous terms appears in "galactose" and "galactan" in the hexose group. The same thing also appears in the use of the specific terms "araban" and "xylan," meaning the specific pentosans which upon hydrolysis yield the pentoses "arabinose" and "xylose." These terms are all established in the literature, and are so rational that it is to be hoped they will not be superseded by such empirical expressions as "furfurose" and "furfurosans."

Purdue University, La Fayette, Indiana, U.S.A.,
January 5, 1895.

A SUBSTITUTE FOR A FUNNEL IN FILTERING LIQUIDS.

By Prof. ARTHUR M. EDWARDS, M.D.,
Late Professor of Chemistry in the Women's Medical College and College of Pharmacy, U.S.A.

Although out of the sphere of teaching chemistry, yet I am in the way of using chemical apparatus, being a geologist, and I still take an interest in chemistry and devise little pieces of apparatus the same as I did over forty years ago when I was assistant to my good friend Dr. John Torrey, at the College of Physicians and Surgeons of Columbia College, New York.

In washing the earths—infusorial earths, as they are called—we have to use filtered water to prevent the minute organisms present in all water from being introduced into the solutions, and thus mar the results arrived at when using the high magnifying glasses of the microscope. Distilled water will not do, for even then the little Diatomaceæ will creep in and puzzle the observer. I have used filters of various kinds, but paper filters are the most convenient. To support them a funnel of glass or similar hard material is used. To facilitate the flow a ribbed funnel has been tried, but this is inconvenient. The flow is too slow, and much of the filter is lost, being left out on account of the adherence of it to the funnel. An upward filter was tried, but that did not answer, being risky and offering a small portion to the flow. At last I did away with the funnel altogether. I now use what I think is a decided advantage. A piece of celluloid, which is collodion mixed with gum camphor, is taken and bent around in the form of a funnel, and placed in an iron retort stand ring. Into this the paper filter can be placed. The celluloid is thin, and can have holes punched in it all over so that it becomes a sieve. Most of the filter can thus be made use of, and when it is not in use the celluloid strip can be washed and put away flat like a sheet of paper.

I am sure this contrivance will be appreciated if it is only tried.

The New Gas, Argon.—At the meeting of the Royal Society on Thursday next, the 31st inst., papers will be read on the "New Gaseous Constituent of the Atmosphere," by Lord Rayleigh and Professor Ramsay, and a description of its spectrum will be given by Mr. Crookes. The reading of the papers will be followed by a discussion, in which it is expected many chemists and physicists will take part. It is our intention to publish in the next day's Chemical News a full report of both papers and discussion.

ON THE GUNNING METHOD FOR TOTAL NITROGEN IN FERTILISERS.

By W. E. GARRIGUES.

Compared to the Scovell-Kjeldahl nitrogen method, that of Gunning, modified to include nitrates, does not seem to have met with the favour that its cleanliness and simplicity would warrant. It is believed that this is, in the main, due to the lower results consequent upon the use of the latter process; hence the following record of an investigation of its merits.

The work was commenced by running parallel analyses on fertilisers of unknown composition, containing sodium nitrate, by both of the methods named. In each case the manipulation, adopted by the Association of Official Agricultural Chemists, was rigidly adhered to. The appended figures, being the results obtained, speak for themselves:—

Kjeldahl with zinc dust. Per cent nitrogen.	Gunning with sodium thiosulphate. Per cent nitrogen.		
3·01	2·40	2·40	
4·98	4·30	4·35	4·55
3·53	3·00	3·10	3·24
4·02	3·50	—	—
4·67	4·05	4·21	4·24

A sample was then prepared from pure sodium nitrate and tankage. The latter was valued by the plain Kjeldahl and Gunning methods and by soda-lime combustion, with the following results.—

Kjeldahl.	Gunning.	Soda-lime.
7·05	7·05	7·08

The calculated content of the mixture was 8·97 per cent nitrogen, about one-half of which was in the inorganic form. On submitting this to analysis there were obtained:—

Kjeldahl.	Gunning.
8·90	7·17
—	7·31
—	7·46

It was very evident that in the writer's hands the Gunning method, as adopted by the Association, did not convert all the nitrogen present into ammonia. After numerous and varied experiments, which, as is usual when viewed in the light of foregone events, now seem to have been largely unnecessary, successful results were finally obtained by using the same reagents, both kind and quantity, but varying the mode and order of their addition.

For convenience of reference the official directions from "Bulletin 38," U.S. Department of Agriculture, are here given:—

"In a digestion flask holding from 250 to 500 c.c. place from 0·7 to 2·8 grains of the substance to be analysed according to the amount of nitrogen present. Ten grms. of potassium sulphate, 5 grms. of sodium thiosulphate, and 30 to 35 c.c. of the salicylic acid mixture, *i.e.*, 30 c.c. of sulphuric acid to 1 grm. of salicylic acid, are then added, and the whole digested at a low temperature until frothing ceases."

The above unsatisfactory, or rather useless, results were obtained in this manner. The chief fault is in the addition of potassium sulphate at such an early stage in the process; the large quantity of dry powder forming an effectual blanket over the sample, that for some time resists the permeation of the viscid acid solution.

The best procedure was found to be:—Adding the salicylic acid mixture directly to the sample in the flask, which is then shaken until the liquid has thoroughly wetted the dry organic matter, allow to stand about fifteen minutes, and add the thiosulphate with constant shaking. This should be done in four or five portions, following with a fresh crystal only when the one previously added has completely dissolved. The potassium sulphate is then put in, and the whole again well agitated. Digest as usual.

Handled in this manner the known mixture above referred to gave:—

8·85
8·87
8·90
8·92

Another sample of dry bone tankage and sodium nitrate was prepared and passed several times through a sixty-mesh sieve. The tankage was valued as before, and showed:—

Kjeldahl.	Gunning.	Soda-lime.
4·32	4·32	4·39
4·40	4·42	—

The calculated content of the mixture was 6·49, and the analyses returned:—

Kjeldahl.	Gunning.
6·45	6·43
—	6·45
—	6·45
—	6·46

Neither method gave results sufficiently accurate for the valuation of sodium nitrate alone; a carefully prepared sample of that salt showing on analysis:—

Kjeldahl.	Gunning.
16·05	15·80
16·35	16·00
—	16·15
—	16·22
—	16·38

Theory, 16·49

It will be noticed that without a single exception the returns of analyses were below the amount actually present. No means of avoiding this loss were found. It would, therefore, seem justifiable to report the highest figure in closely agreeing duplicates instead of the customary average.

Several blanks run through to determine the freedom from nitrogen of the reagents employed gave from nil to 0·05 per cent. No corrections were made for this.

During the distillation in the Gunning process the solution frequently foams badly; so much so, that unless the flame is turned very low, the froth rises into the connecting bulb. The addition of paraffin wax does not always overcome this difficulty, and to avoid it the use of an ordinary 32 ounce wash-bottle, in place of the 500 to 600 c.c. distillation-flask, is recommended.

There is little doubt that the seat of responsibility for many minor discrepancies is imperfect preparation of the sample. Attendant upon the use of the official 25-mesh sieve, variations in the hands of the same manipulator frequently reach 0·15 per cent, even when exceptional care is exercised. It has, therefore, been found advisable in nitrated goods to quarter down the 25-mesh sample to about 2 ounces and pass that through a 60-mesh sieve; when this is done, the difference in duplicate analyses rarely exceeds 0·05 per cent, and decinormal acid and alkali often fail to show any.

Occasionally it becomes necessary to dry the sample before it can be thus finally powdered; in that case making the moisture determinations of Stillwell and Gladding ("Bul. 38," p. 19, U.S. Dept. of Agr.) is the best procedure; *i.e.*, weigh out a portion of about 10 grms. from the original package when first opened, and determine the total moisture in the water-oven, dry the remainder of the sample to dustiness, and prepare it as above; then weigh out two grms. of the fine sample simultaneously with the portion to be used for nitrogen, and ascertain the remaining moisture. A simple calculation brings the nitrogen figure back to the original condition of the goods.

Usually, however, nitrated fertilisers contain only a few per cent of moisture, as indeed they should, lest the free acid of the phosphate in the presence of water act on the easily decomposable salt and liberate nitric acid. This theoretic action has been found a sad reality by manufacturers who incorporated nitrate salts with a wet "super," the loss of plant food being accompanied by a destruction of the fibre of the bagging containing the goods.—*Journal of the American Chemical Society*, xvi., No. 12.

THE RAPID AND ACCURATE ANALYSIS OF BONE-BLACK.*

By W. D. HORNE, Ph.D.

Several years' experience in the analysis of bone-black have led me to the adoption of the following method for attaining accurate results with comparative rapidity:—

In new char, bought from the dealer, the determination of moisture is of importance, being frequently limited by contract to 3 per cent.

In char, in constant use in sugar refineries, the moisture in the revivified sample is of no importance under usual conditions.

The moisture is determined by heating 2 grms. of the unground char for two hours in a hot air-bath at 140° C. It can be weighed between watch-glasses held by a clip to prevent absorption of moisture.

A convenient way of estimating calcium carbonate is with Lunge's nitrometer, using mercury. Two grms. of the finely pulverised sample are introduced into a two-ounce Erlenmeyer flask, and moistened with 3 c.c. of a saturated solution of mercuric chloride, the tube of 10 c.c. of hydrochloric acid (sp. gr. = 1·12) introduced, and the flask closed with a rubber stopper, which, with a short glass tube and a rubber tube, is hung to the tube of the three-way cock. By tipping the acid out upon the char and properly manipulating the stop-cock, the carbon dioxide is liberated, collected, and measured. Any hydrogen sulphide given off is absorbed by the mercuric chloride. Corrections are made for temperature and atmospheric pressure.

For the determination of carbon, iron, calcium sulphate, and insoluble ash, one portion is used. In preparing the sample for analysis, the iron particles must first be removed by a magnet, and the char then ground to an almost impalpable powder.

Two grms. of this are moistened with water and treated in a four-ounce covered beaker, with 20 c.c. hydrochloric acid, and boiled gently until solution is complete, which is within thirty minutes. The beaker is filled up with boiling water, and after settling, which takes place almost immediately, decanted upon a weighed platinum Gooch crucible with asbestos plug. The carbon is washed by decantation in this way five or six times until the filtrate is free from chlorine. The original filtrate and first decanted washing contain practically all of the iron and calcium sulphate. The following wash-waters can usually be rejected. The carbon is washed out of the beaker into the Gooch, and is then washed with 80 per cent alcohol, 95 per cent alcohol and ether, each two or three times, set in a water-jacketed air-bath, and heated at 100° C. to a constant weight, which will take about three hours. The increased weight is due to carbon and ash. The carbon is burned off over the blast. The loss of weight is then carbon, and the difference is ash.

To the acid solution containing iron and calcium sulphate a drop of methyl orange solution is added and ammonia to nearly neutral reaction. Ammonium acetate is added until the solution turns yellow, and then a few drops in excess. The solution is now heated below 70° C. until complete precipitation of iron and aluminum phosphate takes place, which is usually in about twenty minutes. The precipitate, after being washed free from chlorides, is dissolved by dilute sulphuric acid into a six-ounce Erlenmeyer flask, 10 c.c. of a 10 per cent solution of sodium sulphite added, and boiled to reduce the iron and to expel the sulphur dioxide. To ascertain when this gas ceases to come over, the vapour is led from the flask through a glass tube fitting through the rubber stopper and inclining vertically downward at its outer end. Under this is held a test-tube of dilute potassium permanganate acidified with sulphuric acid. So long as sulphur dioxide issues, it will decolourise the permanganate solution in the tube when the gas is caused to bubble up through the upper half inch of the solution. When the sulphur dioxide is all out, a drop of the solution from the flask is tested with potassium sulphocyanide for ferric iron. When the reduction is complete the solution is cooled and titrated with permanganate. If alumina is to be determined, the above-mentioned precipitate of the iron and aluminum phosphates can be treated with 150 c.c. of ammonium molybdate solution to precipitate the phosphoric acid, and filtered. In the filtrate iron and alumina are precipitated as hydroxides by ammonia, filtered off, dissolved in hydrochloric acid, re-precipitated with ammonia, collected, ignited, and weighed. The two may then be separated by any of the well-known methods.

The filtrate from the iron and alumina precipitation contains the calcium sulphate. This solution is acidified with hydrochloric acid, and barium chloride added to precipitate the sulphuric acid. The barium sulphate is treated in the usual way and calculated to calcium sulphate.

Calcium sulphide may be determined by treating 5 grms. of char with 20 c.c. of nitric acid and evaporating nearly dry, adding 20 c.c. of hydrochloric acid, and evaporating again very low to expel nitric acid, taking up in hydrochloric acid, and in an aliquot portion of the filtered solution precipitating the sulphuric acid in the usual way with barium chloride. From the weight of barium sulphate found is deducted that found as above, due to calcium sulphate. The remainder is that due to calcium sulphide.

The physical condition of the char is of great importance, and should be thoroughly examined into. The grist is estimated by throwing 100 grms. upon a sieve of known mesh, shaking gently, and weighing what passes through. This portion may, in turn, be passed through successively finer sieves, and weighed after each. In shaking, the sieve should be tapped only very gently—otherwise particles of char will be forced through which correctly belong above.

To determine the density of the char it should be carefully filled into a weighed flask of 50 or 100 c.c. capacity, and of very gently sloping sides. Admitted into such a flask through a funnel, the char fills it completely without leaving vacant recesses at the shoulders. This is weighed, from which is calculated the specific gravity of the char when loose and the pounds per cubic foot. Now the flask is tapped lightly on the table, and as the char settles down more is added until no further settling takes place, and the flask is filled to the mark. This gives the weight of char when packed, from which may be calculated, as before, the specific gravity and weight per cubic foot.

As char grows old in use its porosity decreases and its specific gravity increases. It is sometimes desirable to know its porosity. To do this the weighed flask is filled with distilled water, the char introduced little by little, displacing part of the water from the flask. At the same time the water remaining displaces from the char its

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* Read before the New York Section, November 9, 1894. From the *Journal of the American Chemical Society*, xvii., No. 1, January, 1895.

contained air, which rises in minute bubbles. The flask is tapped to pack the char, and, when filled to the mark, is heated on the water-bath to expel all air. After cooling, the supernatant water is removed and the flask and contents weighed. The increased weight over that of the flask packed with char is that of the contained water, from which can be calculated the capacity of the char for any liquid of known specific gravity.

The repeated handling which bone-black receives in continued use in sugar refineries, &c., tells on it very seriously, as the friction of the grains against each other and the machinery wears it into dust. This change is slow, but in the long run is very costly, as the fine dust has to be discarded and replaced by new char.

Any method, therefore, which would enable one to judge of the relative durability of samples of char under this continued friction should be worthy of consideration. I have attempted to contrive such a test, and after a good many experiments have found one which promises well. Twenty-five grms. of the char to be tested, between sixteen and twenty-four grist, approximately, are thrown on a sieve with circular holes, one-fiftieth of an inch in diameter, the sieve shaken back and forth ten times, tapped three times, and the shaking and tapping repeated twice. This drives the dust through, and it is weighed. Dust and char are then both put into a cylinder of tinned iron four inches in diameter and two inches deep; then six glazed porcelain marbles five-sixths of an inch in diameter and weighing together 74·66 grms. are added. Now the can is shaken back and forth with slightly rotary motion 200 times, the marbles removed, and the char sifted as before. The increased weight of dust is calculated to per cent of the char used. These tests are pretty constant for different portions of the same sample of char.

The dust formed thus from a good new char was in three cases 1·72 per cent, 1·46 per cent, and 1·76 per cent. From another new char 2·68 per cent and 2·44 per cent. Two grades made by one firm gave 2·16 per cent and 2·16 per cent in one case, and 2·86 per cent and 2·87 per cent in the other. Char which had been in use ten months and whose softer parts had already been separated by use, gave 0·92 per cent and 0·94 per cent, showing that it was then in a better wearing condition than when it first entered into use.

THE PURIFICATION OF POTABLE LIQUIDS.

The distinguished French chemist M. Maumené has been experimenting on the disinfection of drinking-waters, wines, spirits, and saccharine juices. In his operations he makes use of potassium permanganate. This substance certainly burns up a number of the organic impurities present in drinking-waters, &c., and it has the decided advantage of being harmless in any quantity likely to be ingested.

M. Maumené's method is extremely simple. It consists in the use of a dilute solution of potassium permanganate (15·8 grms. to 1000 c.c. of water) in greater or smaller quantity according to the amount of impurity to be destroyed. In from fifteen to twenty minutes the solution in question, say of beet-sugar, loses its characteristic flavour and is rendered pure. Brandies and even wines may be freed in the same manner from unpleasant tastes.

At the meeting of the Chemical Society of Paris on December 5th ult., there ensued a discussion on the novelty as well as the sanitary admissibility of Prof. Maumené's process, for which a patent seems to have been obtained. It was recognised that potassium permanganate has long been in use for determining the organic impurities in waters, and no less in the purification of sewage in grossly polluted waters (in the Thames and elsewhere). But the inventor argued that the final purification of drinking-water in this manner had not been attempted.

Here, however, he seems to be mistaken. In 1873, when preparations were being made for the Ashantee war, Mr. Crookes (Chemical News, November 21, 1873) was requested by the Army Medical Department to suggest a mode of protecting our troops against the use of the highly impure waters of the Gold Coast.

After some experiments on polluted waters he recommended as an addition to the impure water the following mixture:—

Calcium permanganate..	1 part.
Aluminium sulphate	10 parts.
Fine clay	30 ,,

This mixture, in the proportion of 1 c.c. to 10,000 parts even of London sewage, effects a rapid purification.

The addition of the other ingredients along with the permanganate has the object of expediting the process and of precipitating other impurities and living organisms upon which permanganate alone has no immediate action. It was found that moving organisms survived for more than a day in an intensely red solution of permanganate. This latter fact, however, though it shows that permanganate is of little use for soldiers on the march, does not disqualify it as an addition to the reservoirs and clarifying beds of a municipal water supply.

CONTRIBUTIONS TO VOLUMETRIC ANALYSIS.*

By B. REINITZER.

(Concluded from p. 32).

The burette is held with two fingers freely suspended by its upper end against a remote background brightly illuminated, with the lowest level of the liquid at an equal height with the eye looking towards it. The closed fingers of the other unoccupied hand are moved slowly upwards close behind the burette towards the lower curved limit of the liquid until it appears to have a sharply defined black limit. We then read off. It will be perceived that this is the method of reading off described by Mohr against a background half white and half black, so modified that the graduated reading paper which he recommends is dispensed with as not suited for rapid work. By its means the parallactic error is as good as entirely avoided, and readings can be given with full certainty up to 0·02 c.c.

If in a solution to be titrated the neutral-point is found by repeatedly letting off acid and alkali, after some practice and a due observance of the above rules results may be obtained which do not vary by more than 0·02 c.c.

Differences of 0·03 c.c. in the readings effect on using 50 c.c. of acid deviations of 0·0006 in the correction number. For accurate work the temperature of the standard liquids must not be disregarded. 50 c.c. at 17°, if heated to 22°, expand to 50·05 c.c., involving an error in the correction number; or, otherwise expressed, a soda which, if titrated at 17°, shows 100 per cent, if determined with the same acid at 22°, will have apparently 100·10 per cent. As in the rooms of the manufactory the winter and summer temperatures may vary by quite 10°, an acid standardised in summer will in winter show the strength of the soda as 0·2 per cent too low.

DIAZOACETIC ESTER AND PICRIC ACID.

By EDUARD BUCHNER.

The identification of the diazo-compounds of the fatty series has gained practical interest of late in consequence of Von Pechmann's fine discovery of gaseous diazomethan. It may therefore be permissible briefly to refer to a reac-

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* *Zeitschrift Angewandte Chemie.*

tion observed some time ago, which in the case of diazoacetic ester at least renders it possible to obtain a well-crystallised derivative in a very simple manner.

If picric acid is introduced into diazoacetethylester, it passes into solution with a liberation of nitrogen. It is first refrigerated with water; after about one-half mol. has been added to one mol. of the diazo-compound, the product of the reaction is heated in a reflux condenser, and alcohol is added simultaneously, as otherwise there occurs a premature crystallisation of the new compound. Not quite a mol. of picric acid is added. The product congeals on cooling; the crystals are drained and twice re-crystallised from boiling alcohol or precipitated from alcohol by the addition of water.

There result yellowish needles, melting at 102°, which on analysis have the expected composition of trinitrophenylglycolic ethylester, and have the composition $C_{10}H_9N_3O_9$. Potassium picrate is formed from this compound by aqueous potassa-lye on prolonged contact even in the cold. Hydrazin hydrate yields, with liberation of heat, a reddish blue trinitrophenyl hydrazin, which after once re-crystallising from boiling alcohol is obtained in dark prisms of a blue metallic lustre, decomposing at 176°. Here the picric acid behaves with the diazo-compound exactly like the mineral acids; it expels the nitrogen from the diazoacetic ester exactly as it expels carbon dioxide from the carbonates.—*Berichte*, xxvii., p. 3250.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending December 31st, 1894.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, January 10th, 1895.

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 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.

Of the 168 samples examined, one was recorded as "clear but dull," the remainder being clear, bright, and well filtered.

The state of the river has now assumed its normal cold weather condition, and the effect of the floods of last month is imperceptible. Compared with the November figures those of December show a marked improvement in almost every particular in the Thames-derived waters. The common salt and the hardness are slightly increased consequent on the less dilution. The nitric acid is also greater, showing that the oxidation of nitrogenous matters present is effective and abundant. The oxygen required to oxidise the organic matter present is much less than before, and the organic carbon has sunk from 0·260 grain per gallon in November to 0·156. The filtration leaves little to be desired, only one sample of the 168 examined being recorded as clear but dull.

We have taken frequent samples from the different standpipes for bacteriological examination. This affords a certain guide as to the proper working of the filters. If the bacteria in any particular sample of water show signs of approaching the limit which is permissible in pure drinking water, immediate notice will be sent to the Company, so that the imperfectly filtered supply can be cut off from the distributing mains, and the defective filter remedied. The necessity for such a notice has, however, not yet arisen, as the bacteria have been very low during the month, the highest number not reaching to within 75 per cent of the permissible amount.

Special samples have also been taken from the general shafts at the different water works. The number of bacteria here have been uniformly low, the average being 30 per c.c.

The rainfall in the Thames valley has been a little above the 25-year average. The actual fall has been 2·39 inches, while the average fall is 2·10, showing an excess of 0·29 inch.

The rainfall for the year 1894 has been in excess of the average, as will be seen from the following tabular statement:—

Table Showing the Rainfall in Inches at Oxford, Month by Month, during the year 1894.

	Actual fall.	Mean of 25 years.	Deficiency.	Excess.
January	1·74	2·26	0·52	—
February	1·60	1·92	0·32	—
March	1·67	1·59	—	0·08
April	1·70	1·78	0·08	—
May	1·45	1·95	0·50	—
June	2·79	2·21	—	0·58
July	3·27	2·38	—	0·89
August	2·48	2·24	—	0·24
September.. ..	1·74	2·66	0·92	—
October	3·97	2·56	—	1·41
November.. ..	4·80	2·31	—	2·49
December.. ..	2·39	2·10	—	0·29
	29·60	25·96	2·34	5·98

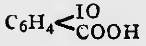
There is therefore an excess of 3·64 inches, the whole of which has fallen since the middle of October, up to which date the fall has been below the average.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

ON A NEW CLASS OF CYCLICAL IODINE COMPOUNDS OF THE IODOSO-GROUP FROM IODOPHENYLACETIC ACID.

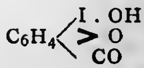
By WILHELM RAUM.

Victor Meyer and his associates have shown that the ortho-iodobenzoïc acid can easily be converted into ortho-iodosobenzoïc acid by oxidising agents. This acid, as was shown by Meyer and Wachter as early as the discovery of iodosobenzoïc acid, appears in the tautomerous forms,—



$C_6H_4<\begin{matrix}IO\\COOH\end{matrix}$

and



$C_6H_4\begin{matrix}/I.OH\\>O\\\backslash CO\end{matrix}$,

according to the constant tendency to the production of a pentamerous ring.

At the instigation of Prof. V. Meyer, I have investigated the behaviour of orthoiodophenylacetic acid, $I.C_6H_4.CH_2.COOH$, in which possibly the production of a ring of six members might be expected.

For comparison I have also examined the isomeric para-acid.

Production of Orthoiodophenylacetic Acid.

This acid was obtained by Mabery and Robinson. I obtained it also by dropping bromine into orthoiodotoluol heated to 200° and further elaboration of the bromide.

I used, however, a simpler method of purification than did the authors above named. 100 grms. ortho-toluol were heated to 200° on the oil-bath fitted with a reflux condenser and a dropping-funnel, and in the course of about half an hour the requisite quantity of bromine was dropped in. The product was washed, freed from uncombined iodine, and distilled along with watery vapour. At first there passed over an oil and then a crystalline mass. This was dissolved in hot ligroine, and the solution cooled in a freezing mixture, when splendid white crystals separated, melting at 54°. They are pure *orthobenzylbromide.*

This substance attacks the mucous membrane in an unbearable degree. When working with it the hands must be protected with caoutchouc gloves, as otherwise there occurs a violent eruption.

It was now converted into the nitrile by heating it for four hours in an alcoholic solution along with potassium cyanide. The nitrile is saponified with fuming hydrochloric acid, and the acid obtained is re-crystallised from much hot water. It crystallises in colourless needles melting at 106°—108°. Its composition is $C_6H_4I.CH_2.COOH$.

Mabery and Robinson give the melting-point as 95—96°. The second crystallisation of the crude acid has a more yellow colour, and melts below 100°.

Perfectly pure orthoiodophenylacetic acid, which I afterwards obtained by decomposing the iodide-chloride, melts at 110°.

For transformation into iodoso-acid, I had to use the indirect method by way of the iodide-chloride, as the direct oxidation would probably have converted the group $OH_2.COOH$ into carbonyl.

The chloride is easily obtained by introducing chlorine into the dilute solution of the acid in chloroform (3 parts of the acid in 20 of chloroform). It forms yellow crystals containing, by titration with potassium iodide, 20·9 and 20·93 per cent of active chlorine. By concentration, 21·32 per cent.

In contact with cold water the chloride loses its yellow colour. If it is ground up with water and allowed to stand for some time we obtain a white powder, which is produced in a state of purity by washing, draining on clay, drying, and extraction with ether. It melts with decomposition at 119°, and is strongly active with potassium iodide.

A volumetric determination of the iodine liberated gives 83·94 and 83·5 per cent of iodine.

This liberation of iodine would correspond to 5·29 and 5·26 per cent of active oxygen. Iodosophenylacetic acid would therefore contain theoretically 5·76 of active oxygen.

The substance contains a considerable proportion of chlorine.

The determinations of the halogens according to the method of Carius showed that the iodide-chloride gives off 1 mol. hydrochloric acid by the action of water, yielding a compound, $C_8H_6O_2ClI$.

It might, according to its composition, be regarded as a mixture of iodide-chloride and iodophenylacetic acid. But its total behaviour shows that such is not the case. It is insoluble in ether, in which the two substances named readily dissolve. A microscopic examination shows the absence of the splendidly crystalline orthophenylacetic acid, which is present to a small extent in the crude substance not yet washed with ether.

Hence a chloride has been formed which takes a mean place between an orthoiodoso-compound and an iodide-chloride. As it was expected, it contains an hexamerous ring. Representatives of this new class of substances have repeatedly been observed in this laboratory.

Experiments with Paraiodophenylacetic Acid.

From this acid I have hitherto not obtained an analogous substance.

If the iodide-chloride of the acid is boiled with water we obtain pure paraiodophenylacetic acid, as also when the iodide-chloride is dissolved in an excess of soda-lye and then acidified. On grinding up with cold water, the chloride is only very slowly attacked. Hence there does not exist an analogue of the new substance in the *para*-series, or it is formed much less readily than its isomer.

The investigation is being continued.—*Berichte*, xxvii., p. 3323.

ON THE QUALITATIVE SEPARATION OF NICKEL AND COBALT.

By A. VILLIERS.

The very distinct differences found in the action of sulphuretted hydrogen upon the salts of nickel and of cobalt may be utilised for the qualitative detection of the smallest quantities of nickel in presence of a very large excess of cobalt.

The liquid which may contain these two metals is mixed with tartaric acid and a large excess of soda (not potassa). The addition of tartaric acid is to hinder the precipitation of the metallic oxides by the alkali. It is then submitted to the action of a current of hydrogen sulphide until completely saturated (this last condition being necessary to effect the complete precipitation of the cobalt), and it is filtered immediately. In the entire absence of nickel the filtrate is quite colourless. It is only after the lapse of a considerable time that it turns yellowish by the action of the air owing to the liberation of sulphur. The presence of nickel, on the contrary, is indicated by the colouration of the filtrate, which is black if the nickel is in a considerable quantity, brown if it is less, but precipitable even if there are traces. We may thus detect the presence of nickel in a great number of commercial salts of cobalt, sold as pure. If we add a few thousandth parts of a salt of nickel to a pure salt of cobalt, the reaction is very distinct. It is therefore very sensitive, and can be applied in a few minutes.

The separation of cobalt sulphide determines a removal of a fraction of the nickel in proportions which vary with the dilution of the liquid. Inversely a certain quantity of cobalt remains in solution in a liquid containing a large excess of nickel. Thus we have not been able hitherto to utilise the above reaction for the quantitative separation of the two metals.

Salts of ammonia must not be present, and must be previously removed if necessary, as also metals precipitable by hydrogen sulphide in an acid solution or by ammonia in an acid liquid, and by ammonia in presence of ammonium chloride (after the peroxidation of the iron).

In the general case of the search for metals the filtrate from the precipitates, which may have been produced by hydrogen sulphide or by ammonia, will be precipitated by ammonium hydrosulphate prepared as recently as possible, avoiding the addition of too large an excess of the reagent. The precipitate is treated with very dilute hydrochloric acid at ebullition; the black residue, which may contain nickel and cobalt sulphides, is dissolved in a little aqua regia, and the hydrochloric solution thus obtained is submitted to the test above described after the chief part of the acid has been driven off.

A single cause of error may occur. If there is an extremely small quantity of cobalt, the precipitation of the cobalt sulphide may be hindered by the dilution, and in this case, even in the absence of nickel, we shall obtain a liquid more or less deeply coloured of a light brown. But it is sufficient to add a large excess of soda in order to obtain a complete precipitation and a filtrate perfectly colourless.

The detection of nickel may be effected still more quickly, though with less certainty, by means of the solubility of nickel sulphide in ammonium hydrosulphate, unless the latter contains sulphur in solution.

It is sufficient to pour, into a liquid mixed with ammonium hydrochlorate and ammonia, a large excess of this reagent. The presence of nickel will be shown by the brown colour of the filtrate. But under these conditions the cobalt sulphide begins to dissolve if the quantity of sulphur in solution in the ammonium hydrosulphate is very considerable. It is hence necessary to employ a reagent containing sulphur, but not too much, which would render the reaction uncertain.—*Comptes Rendus*, cxx., p. 46.

DERIVATIVES OF DIAMIDE WITH A CLOSED ATOMIC GROUPING.

By TH. CURTIUS.

Treatise I.—*The Action of Hydrazin Hydrate on certain β and γ Ketonic Acid Esters.*

In this first treatise the author briefly summarises former researches in this direction executed by himself, in concert with R. Jay, with K. Thum, Dr. Hans Lang, Dr. Th. Knœber, and the results of his own unpublished investigations down to the beginning of the researches of Dr. R. Von Rothenburg.

1. *Hydrazin Hydrate and Acetacetic-Acetic Ester.*—The result of the reaction is (3) methylpyrazolon, the preparation and properties of which have been already described by Curtius and Jay.

(3)-*Methylpyrazolon* forms both with acids and bases salts of little stability. (3)-Methylpyrazolon hydrochlorate is obtained by evaporating down an aqueous solution of (3)-methylpyrazolon with hydrochloric acid. In a vacuum the salt cystallises in radiating tufts. It is extremely hygroscopic.

(3)-Methylpyrazolon dissolves easily in dilute aqueous ammonia. The salt is permanent only in a dilute aqueous solution. With silver, mercury, lead, manganese, and copper salts it yields sparingly soluble precipitates.

(1)-Acetyl-(3)-methylpyrazolon is formed by the action of acetic anhydride upon (3)-methylpyrazolon, $C_6H_8N_2O_2$. It crystallises from very dilute boiling alcohol in long colourless needles melting at 140°. It is insoluble in ether and benzene, sparingly soluble in cold alcohol and ether, but more soluble on the application of heat. It is rapidly decomposed by both solvents on ebullition, acetic acid or acetic ester being split off. It behaves like a feeble acid.

(4)-*Isonitroso*-(3)-*methylpyrazolon*, $C_4H_5N_3O_2$, is obtained by passing off the red vapours (evolved from the action of nitric acid upon arsenic) into an aqueous solution of (3)-methylpyrazolon. It may also be obtained by the action of a mol. sodium nitrite upon the acetic solution of pyrazolon. It crystallises from water in yellowish silky needles, fusible at 194°, and is readily soluble in cold water and alcohol. It behaves like a powerful acid. Its aqueous solution is at once precipitated by platinum chloride, mercuric chloride, and silver nitrate. These salts have yellow to red colours.

(4)-*Isonitro*-(3)-*methylpyrazolon* silver has the composition $C_4H_4N_3O_2Ag$. It crystallises from hot glacial acetic acid in small dark red needles, which begin to decompose above 130°. If rapidly and strongly heated they detonate, giving off hydrocyanic acid.

The solution of isonitrosopyrazolon silver in glacial acetic acid is reduced by zinc powder, but (4)-amido-(3)-methylpyrazolon is not obtained.

(3)-*Methylpyrazolon*-(4)-*isonitroso ethylester*, $C_6H_9N_3O_2$, is obtained by the action of iodethyl upon the dried silver salt. The combination is explosive.

(4)-*Benzol*-(3) *methylpyrazolon* has the composition $C_6H_9N_3O_2$. (4) - Benzol - (3) - methylpyrazolon, represented by the formula $C_{10}H_{10}N_2O$, is obtained, by heating (3)-methylpyrazolon with an equi-molecular quantity of benzaldehyd. It dissolves in the liquid with a deep reddish yellow colour. It melts at 204°. It is insoluble in water, very sparingly soluble in ether or benzene.

Hydrazin Hydrate and Benzoylacetic Ester. — The reaction of these substances yields (3)-phenylpyrazolon, $C_9H_8N_2O$. It crystallises from alcohol in stout, colourless prisms, which melt at 236° with decomposition. It is almost insoluble in cold alcohol, ether, or benzene, but it is taken up to a considerable extent by boiling alcohol. With acids and bases it behaves quite like the methyl compound.

(1)-*Acetyl*-(3)-*phenylpyrazolon.*—This substance is obtained by the action of acetic anhydride in a manner quite analogous to the corresponding methyl compounds. The product after drainage by suction is rapidly re-crystallised from hot alcohol. Its composition is represented by the formula $C_{11}H_{10}N_2O_3$. It crystallises from dilute alcohol in stout, colourless prisms, fusible at 121°. It is sparingly soluble in cold alcohol and water, also in ether and benzene. The solutions are gradually decomposed with abscission of acetic acid.

The aqueous solution of the acetyl compound gives a white precipitate with silver nitrate.

(4)-*Isonitroso*-(3)-*phenylpyrazolon* is formed as a reddish precipitate on dissolving phenylpyrazolon in alcohol and introducing nitrous vapours. The precipitate on re-crystallisation from hot water forms long fine yellow needles.

(3)-*Methyl*-(4)-*pyrazolon acetic ester* is obtained at once by the action of hydrate upon acetsuccinic-ester, with the abscission of water and alcohol.

(3)-*Methyl*-(4)-*pyrazolon acetic ethylester* crystallises from alcohol in leaflets of a silvery lustre, but from water in large colourless tables which melt at 166° without decomposition. The substance is easily soluble in both liquids in heat. In benzene or ether it is sparingly soluble. If nitrous acid is introduced into the aqueous solution it gives a yellow nitroso compound.

IV.-*Hydrazin hydrate* acts upon diacetsuccinic ester very differently, according as 1 mol. or 2 mols. are caused to react with the compound. If 1 mol. diacetsuccinic ethylester is dissolved in about 10 parts of alcohol with the addition of 2 mols. hydrazin hydrate, the mixture heats spontaneously and deposits abundance of a crystalline powder sparingly soluble in almost all media. The composition of this substance is $C_4H_5N_3O$.

If 1 mol. hydrazin hydrate acts upon 1 mol. diacetsuccinic ester we have a compound of the calculated composition $C_{12}H_{18}N_2O_4$.

Levulicester and Hydrazin Hydrate.—Pure levulicethylethylester was diluted with one volume alcohol and gradually mixed with one mol. hydrazin hydrate. The reaction is quickly completed. When cold a colourless substance separates out in shining leaflets, and is purified by re-crystallisation from water. Its composition is $C_5H_{10}N_2O_2$. It may be regarded as β-acetylpropionhydrazid.

Levulichydrazid crystallises from water in large thick colourless prisms, fusible at 82°. It is moderately soluble in cold water or alcohol, less so in ether or in benzine. It is both an acid and a base. If heated above its melting point it loses a mol. of water and forms an anhydride in which an annular constitution can be recognised.

Hydrazin levulic anhydride = (3)-*methylpyridazinon* (formerly named by the author (3)-methylpyridazolon) is obtained from the hydrazid, at first obtained by heating a calculated quantity to 120° in the oil-bath. It crystallises from benzene in nacreous leaflets, fusible at 94°. It distils without decomposition at the ordinary atmospheric pressure. It appears as a homologue of (3)-methylpyrazolon.

The instability of this pyridinon ring is remarkable as compared with the striking stability of the pyrazolon ring (3)-phenylpyridazinon-(5)-carbonester.

β-Benzoylisosuccinic acid in an alcoholic solution was treated with gaseous hydrochloric acid with refrigeration. If the solution after standing for some time is poured into water, the ester separates out as a dark coloured oil. It was taken up with ether and shaken repeatedly, first with very dilute sulphuric acid, then with dilute soda lye, and lastly with water. The ethereal solution desiccated by calcium chloride leaves, after evaporation on the water-bath, very pure β benzoylisosuccinic ethylester as a pale yellow liquid.

Hydrazin hydrate acts upon an equi-molecular quantity of the ester thus obtained, forming (3)-phenylpyridazinon-(5) carbonic ester. It crystallises in long colourless needles of a silky lustre, fusible at 156°, moderately soluble in cold alcohol, readily in hot alcohol and hot water, sparingly soluble in ether. It is not reduced by boiling with Fehling's solution. If heated with sulphuric acid hydrazin salt is split off.

(3)-*Phenylpyridazinon* (5)-*carbonic acid*, $C_{11}H_{10}N_2O_3$, separates from hot water as a colourless crystalline powder, fusible at 116°—117°, and is decomposed at slightly higher temperatures with abscission of carbonic acid.

(3)-*Phenylpyridazinon* (5) *carbonic hydrazid*.—This substance can be obtained from the ester above described by heating hydrazin hydrate, with the abscission of alcohol. Its composition is $C_{11}H_{12}N_4O_2$; it crystallises from hot alcohol in long splendid colourless prisms, which about 190° turn brown and are decomposed. It dissolves readily in hot water and alcohol, but is insoluble in ether and benzene. It behaves like an acidylhydrazide. On heating it reduces Fehling's solution.

Hydrazin Hydrate and β-Benzoylpropionic-ester.—These substances react with the formation of phenylpyridazon.

This substance crystallises from alcohol in stout colourless long columns, but from water in fine shining needles, fusible at 149°—150°. The crystals are sparingly soluble in cold water and ether. It has a neutral reaction, and is decomposed with difficulty on boiling with dilute sulphuric acid with the abscission of hydrazin salt. It is very stable with alkalies. It does not attack Fehling's solution even in heat.

The investigation on the action of hydrazin hydrate on the ketonic esters is being continued.

(To be continued).

THE SECRET OF THE BROWNIAN MOVEMENTS.*

By R. MEADE BACHE.

We first hear systematically of molecular movement, as a thing directly visible, from the writings of the distinguished botanist, Dr. Robert Brown, embodied in a paper entitled "A Brief Account of Microscopical Observations, made in the Months of June, July, and August, 1827, on the Particles contained in the Pollen of Plants; and on the General Existence of Active Molecules in Organic and Inorganic Bodies."

Of course we know inferentially, through physics and chemistry, that the particles of bodies move under the influence of various extraneous forces, and we know, too, that in the case of matter in a gaseous form they move also under the influence of force inherent in their own constitution. But the movements of which I am about to speak relate to the visible behaviour of what should be termed inert matter, if that expression were not begging the question of whether or not it has in itself power of motion, and thus deciding it in favour of the view that it has not, but is moved by extraneous force. We must begin, therefore, as is but right, by assuming that it is an open question as to whether or not certain particles, in aqueous suspension, call them molecules or otherwise, as one pleases, organic or inorganic, but not endowed with animal life, are of themselves capable of movement, or are moved by some extraneous force or forces at present unknown. The solid ground of fact from which we start is that, under the conditions mentioned, they do move, for that is undeniable and admitted.

Dr. Brown soon discarded, through disproving in the course of his investigations the surmise which he had made, that the particles of pollen indicated by their motion a mode of function analogous to that of spermatozoids, and rested eventually in the conclusion that particles moving in aqueous solutions are not confined to organic bodies or to their products. He had conducted a series of experiments on finely crushed glass, on simple earths and metals, with many of their combinations, and rocks of all ages, including those in which no organic remains have ever been found. Moving particles presented themselves in each of the constituent minerals of granite. Even a crushed fragment of the Sphynx gave the same results. He tried substances of both aqueous and igneous origin, travertine, stalactites, lava, obsidian, volcanic ashes, meteoric matter, manganese, nickel, plumbago, bismuth, antimony, arsenic, asbestos, actinolite, tremolite, zeolite, and steatite. He tried particles of wood, living and dead, linen, paper, cotton, silk, wool, hair, and muscular fibre that had been exposed to fire under the blowpipe, douched with water, and submitted to immediate examination. The particles from all these substances exhibited as vivid movement after, as before, they had been so treated.

Dr. Brown, about twelve months later, went on further to declare, under the head of "Additional Remarks on Active Molecules," that: "The result of the inquiry at present essentially agrees with that which may be collected from my printed account, and may be here briefly stated in the following terms: namely, that extremely minute particles of solid matter, whether obtained from organic or inorganic substances, when suspended in pure water, or in some other aqueous fluids, exhibit motions for which I am unable to account, and which, from their irregularity and seeming independence, resemble in a remarkable degree the less rapid motions of some of the simplest animalcules of infusions. That the smallest moving particles observed, and which I have termed active molecules, appear to be spherical, or nearly so, and to be between 1-20,000 and 1-30,000 of an inch in diameter; and that other particles of considerably greater and various size, and either of similar or of very different figure, also present analogous motions in like circumstances. I have formerly stated my belief that these motions of the particles neither arose from currents in the fluid containing them, nor depended on the intestine motion which may be supposed to accompany its evaporation. These causes of motion, however, either singly or combined with others,—as the attractions and repulsions among the particles themselves, their unstable equilibrium in the fluid in which they are suspended, their hygrometrical or capillary action, and in some cases the disengagement of volatile matter, or of minute air bubbles,—have been considered by several writers as sufficiently accounting for the appearance. Some of the alleged causes here stated, with others which I have considered it unnecessary to mention, are not likely to be overlooked or to deceive observers of any experience in microscopical research; and the insufficiency of the most important of those enumerated may, I think, be satisfactorily shown by means of a very simple experiment." (Dr. Brown here alludes to what he details at considerable length, as to the trituration together of oil and water, so as to secure, in one case, by a large proportion of water to oil, lacunæ of water of various sizes, filled with particles, protected from evaporation by the oil, and in the converse case, by a small proportion of oil to water, to secure minute oil drops on the surface of the water, some of

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* Read before the American Philosophical Society, April 20, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

which drops were not larger than the solid particles in the water).

These passages from the writings on this subject of so skillful, careful, and conscientious an observer as Dr. Brown was, excite regret that he had not pursued the subject further. He would have found, among other things, a much simpler and more lasting method of excluding air from the drop under observation, than that which he adopted in forming lacunæ of aqueous fluid protected from evaporation by immersion in oil. He would in all probability have discovered the real cause of the motion of organic and inorganic particles in aqueous fluids. But he dropped the subject, perhaps because he was obliged so to do on account of the pressure of other research, when he had obtained some valuable results, leaving his investigations negative as to conclusions. He doubtless began with the supposition, which seems common at first to all investigators of the subject, that evaporation might represent a shock that would move the particles suspended in water; that vibration from mechanical sources might account for the movements; that currents set up in the drop of water by differences of temperature in it or slight differences in the temperature of the air surrounding it, might account for them; or that mutual attractions, derived from gravitation, and inherent in the relative density of the particles themselves, might do so; and he found, as everyone else will find who experiments in these directions, that the movements go on independently of currents and independently of heat, generating or not generating currents, independently of light, and in the case where the particles represent an extremely fine division of matter, and are at the same time of low specific gravity, even independently of terrestrial gravitation; and without relation to their specific gravity, with the force of their mutual gravitation entirely masked.

Some of these things Dr. Brown implies that he saw in the course of his investigations; others he could hardly have failed incidentally to see, but one that I have mentioned he did not rightly interpret. It was a distinct lapse in his acuteness of observation, that involved in his mention, without perception of its deepest significance, of minute drops of oil, some of them not exceeding the solid particles themselves in size, standing nearly or altogether at rest on the surface of water; the pointing of which fact is very clear, one which, had it been known to me, would have induced me to try oil as well as water among the first instead of among the last of my own experiments, as actually happened in their sequence.

To afford facility for the fullest comprehension of the subject, it becomes proper here to resume the historical tenor of our way with a brief account of some of the views of Herren Wiener, Exner, and Schultze, more recent than those of Dr. Brown. In order to avoid the responsibility for the necessary condensation, I prefer to quote, as follows, from the summary of their views in the *Jahresberichte* of 1867:—

"Then Chr. Wiener, from whose account the preceding historical remarks are quoted, instituted microscopic observations of these movements, and came to the conclusion that this trembling, irregular, unsteady motion of solid molecules, which alter their direction in the briefest fraction of time in their zigzag course, has for its basis the continual movements which, by virtue of their molecular constitution, belong to fluids. He learned through his investigations (1) that the movements are not those of infusoria; (2) that the movement is not communicated to the fluid; (3) that the trembling movement is not in any way derived from the varying attraction and collision of the various oscillating molecules with one another; (4) that the movement is not derived from changes of temperature; (5) that, also, the movement is not derived from evaporation. Consequently there remained to him nothing to ascribe as the cause of the peculiar movements but the property of the fluid itself. This explanation received direct confirmation from Wiener's observation, that the amount of the movement has a certain relation to the size of the molecule. Lately S. Exner has extended the investigations of Wiener. Among the various influences which Exner sought to test with reference to the molecular motion was whether either chemical causes or mechanical ones, such as pressure, vibration, and so forth, could in any way produce an acceleration or a retardation of the effect. Only by exposure to light and heat did the motion become accelerated, and then in such a manner as, in the case of glycerin, the molecules of which under ordinary conditions show scarcely any, if any movement at all, to exhibit it clearly when warmed up to 50° C. of temperature. Exner also examined into the properties of fluids in which solid molecules remain suspended. The results of his investigation resolve themselves into the following points:—(1) The liveliness of the molecular movement is heightened by light and heat, and by radiant as well as by conducted heat; (2) one of the consequences of the molecular movement is that the molecules, in a specifically lighter fluid, not only do not sink to the bottom, but overcome the force of gravitation to such a degree as to spread themselves equally throughout the fluid; (3) the velocity of this scattering is as the intensity of the molecular movements influenced by light and heat. It should be mentioned here that Fr. Schultze had already stated that substances, when most finely divided, especially such as seemed under the microscope to be amorphous, and exhibited the brownian movements, remain suspended in pure water and in many other fluids for days, weeks, and months at a time, so that the fluid containing them presents a cloudy, or at least an opalescent appearance."

(To be continued).

PROCEEDINGS OF SOCIETIES.

UNIVERSITY COLLEGE, LONDON, CHEMICAL AND PHYSICAL SOCIETY.

January 16th, 1895.

"*On Opium*." By Robert D. Littlefield.

The first paper of this term was given on Wednesday, January 16, and dealt with the history, cultivation, and constitution of opium gum. In the course of his remarks the lecturer referred to ancient records of opium, mentioning Scribonius Largus, A.D. 40, who gave an account of opium preparation, and Dioscorides, A.D. 70, who recorded the fact of the juice of the whole opium-bearing plant being less active than that made only from the juice of the capsule; and later Pliny, who, in addition to noting its preparation, describes its medicinal use. In ancient Latin records reference is made frequently to *Lachrima papaveris*, indicating that at that time even opium was looked upon as a most valuable drug.

Concerning the cultivation, an explanation of the formation of the latex in the plant was given, and the general manner in which the capsule was incised, the juice scraped off, and collected. The plant, as cultivated in Asia Minor, usually has white or purple flowers, and blooms in May to July according to the elevation of the land.

A naturally rich and moist soil is necessary, and a drought, frost, or locust-pest may wreck a good healthy plantation.

The opium specimens shown—kindly lent by Messrs. Hearon, Squire, and Francis—were then explained, the various characteristics being shown distinguishing the Asia Minor, Turkey, Persian, Egyptian, and Indian varieties. The peculiar narcotic bitter smell and taste were pointed out, and concerning the constitution the lecturer said that, roughly speaking, half a sample of opium consisted of albumen, fruit juice, gum, fragments of leaves, and rubbish, and the remainder contained the alkaloids, sugars, and, according to Hesse, some wax.

The acids present are sulphuric, phosphoric, and the one peculiar to the poppy, meconic. The inorganic bases are potassium, magnesium, and calcium oxides. The list of alkaloids in opium hitherto found, though very great (some 20 or so) was possibly not yet complete. Some were entirely absent from samples of the gum, and if present were only there in minute traces.

Morphine and its derivative apomorphine (discovered by Matthiesen and Wright), codein, and narcotin were the principal ones. The method of estimating the morphine in opium, as given by the British Pharmacopœia, was explained. The morphia existing in the opium as sulphate and meconate is soluble in excess of calcium hydrate.

This solution is treated with S.V.R. and ether in certain proportions, and the addition of ammonium chloride causes the precipitation of the morphia (being insoluble in the S.V.R. and ether mixture), whereas other organic substances which the NH_4Cl throws out were soluble, so that the morphia is obtained in a practically pure state, and can be weighed after the necessary drying.

After reference to apomorphine some tests for morphia were shown, and emphasis was laid on the reaction of neutral ferric chloride on an aqueous solution of opium, the beautiful red-coloured solution (that of meconate of iron) being unaffected by mercuric chloride. This being an almost conclusive test for meconic acid inferred the presence of opium in the solution tested.

In a discussion which ensued, Dr. Norman Collie referred to the ferric chloride test; he stated that some of the acetone-acetyl derivatives gave this colour exactly, and that this fact very possibly indicated the presence of this organic group in the formula of meconic acid.

Mr. Das also mentioned the effect and use of opium smoking and eating in Northern India. He remarked that there was a belief that the use of the drug was beneficial in preventing the severity of the malarial attacks and also the intensity of poisonous snake bites.

CORRESPONDENCE.

ESTIMATION OF PHOSPHORIC ACID IN THE PRESENCE OF LIME.

To the Editor of the Chemical News.

Sir,—I am not aware whether it is generally known that phosphoric acid may be estimated by the citro-magnesic method without removal of the lime.

The enormous saving of time effected by this means will be appreciated by every operator who tries this method. The results obtained are quite as accurate, in fact, I believe, more so, than when the lime is removed previous to precipitation.

The method is particularly applicable to ferruginous manures, and should then be wrought in concentrated sol.—I am, &c.,

J. G. A.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 27, December 31, 1894.

Study of the Graphites of Iron.—Henri Moissan.—The author has proved that a great number of metals, such as aluminium, platinum, chromium, uranium, vanadium, &c., can dissolve carbon when the temperature is sufficiently high, and abandon it again in the state of graphite. On studying the conditions under which graphite is formed in one and the same metal, iron, on varying the temperature and the pressure, he has reached the following results:—1. At the ordinary pressure graphite is the purer the higher the temperature at which it is formed. 2. This graphite is so much the more stable in presence of nitric acid and potassium chlorate the higher the temperature at which it has been produced. 3. Under the influence of pressure, the crystals and the masses of graphite take the aspect of a fused matter. 4. The small quantity of hydrogen which graphites always contain decreases distinctly as their purity increases. A graphite which has not been treated with any reagent, and which has been previously heated in a vacuum, does not form water on its combustion in oxygen. 5. On attacking cast-iron with acids there are produced hydrogenous and oxygenous compounds which resist a dull-red temperature, and which, like graphite, are destroyed on combustion.

Nomination of a Correspondent for the Mineralogical Section.—M. Richthofen was elected to fill the place in this section left vacant by the decease of Kokscharow, receiving 33 votes, against 3 given to Rütimeyer, and 2 given to Tschermac.

Nickel and Cobalt Sulphides.—A. Villiers.—If we bring in contact a precipitate of nickel sulphide and ammonium sulphide there is occasioned partial solution, shown by the colour of the filtrate. The colour is very intense if the ammonium sulphide is strongly charged with sulphur. If the reagent is absolutely free from sulphur, and secured from contact of air during filtration, the totality of sulphide remains on the filter, and the filtrate is colourless. Precipitates of cobalt sulphide do not dissolve in ammonium or sodium sulphides and hydrosulphates. It is only when the latter contain a large quantity of sulphur in solution that the filtrate has a slight brown colour and contains traces of cobalt.

Calcium Ethylate.—M. de Forcrand.—The author has studied the compound which calcium carbide (CaC_2) forms with absolute ethylic alcohol. The compound is not calcium ethylate, but an addition compound of alcohol and anhydrous lime, of the composition $3CaO+4C_2H_6O$.

On β-Oxycinchonine.—E. Jungfleisch and E. Léger.—If crystallised from strong alcohol, β-oxycinchonine forms small prismatic needles, colourless and anhydrous. It melts at 273°, but begins to be coloured at 250°. It is more dextrorotatory than α-oxycinchonine. It is almost insoluble in water, soluble in cold alcohol, but very soluble in hot alcohol. Acetone dissolves it less freely than its isomers. It dissolves also in chloroform. Its formula is $C_{28}H_{22}N_2O_4$. It is a di-acid base, and forms with monobasic acids two classes of salts: $C_{38}H_{22},N_2O_4A$ and $C_{38}H_{22}N_2O_4,2A$.

Action of Chlorine upon the Secondary Alcohols.—A. Brochet.—The action of chlorine upon the precipitated alcohols of the form $R.CHOH.CH_3$ gives acetones of the form $R.CO.CCl_3$, the radicle becoming chlorinised according to its special affinities.

Industrial Preparation and the Physiological Properties of Nicotine Oxalate and its Crystalline Salts.—H. Parenty and E. Grasset.—This paper requires the accompanying figure. It may, however, be stated that the fatal dose of pure nicotine, which is between 20 and 21 m.grms. per kilo. of the weight of the animal, rises to 70 m.grms. of combined nicotine, or 150 m.grms. of the quadroxalate per kilo. of the animal. The fatal symptoms are the same in both cases.

On the Tar of the Pine.—Adolphe Renard.—The creosote of the pine, as regards its proportion of guyacol, is intermediate between that of the beech and the oak.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., November 5, 1894.

Action of the Electric Arc upon Diamond, Amorphous Boron, and Crystalline Silicon. — Henri Moissan.—Already inserted.

Preparation and Properties of Crystalline Carbon Silicide. — Henri Moissan. — Already noticed under *Comptes Rendus.*

Preparation and Properties of Carbon Boride.—Henri Moissan.—Already noticed under *Comptes Rendus.*

Preparation in the Electric Furnace of a Crystalline Calcium Carbide. Properties of this Novel Substance.—Henri Moissan. — Noticed under *Comptes Rendus.*

Study of the Crystalline Barium and Strontium Acetylides.—Henri Moissan.

Preparation of Crystalline Aluminium Carbide.—Henri Moissan.—Carbon is capable of combining with aluminium, forming a yellow crystalline carbide of the formula C_3Al_4. This novel compound possesses well-marked reductive properties; it decomposes water slowly at common temperatures, giving off methane or formene, CH_4. This is the first instance of a similar decomposition. Perhaps this carbide has intervened in the geological phenomena which have produced for ages discharges of formene.

New Researches on Chromium.—Henri Moissan.—Already noticed under *Comptes Rendus.*

Determination of the Specific Gravity of Melted Magnesia.—Henri Moissan.—In our experiments made in the electric furnace we have always found that magnesia, purified by Schlœsing's process, cannot be reduced by coke. This fact enables us to construct the interior of our furnaces with alternate plates of magnesia and coke, and to utilise magnesia for the formation of our crucibles. The specific gravity of magnesia, after ignition in a wind-furnace for ten hours, was found to be 3·577; that of magnesia which had been exposed for two hours to the action of the arc was 3·589; and that which had been fused in the crucible of the electric furnace 3·654.

Impurities of Commercial Aluminium.— Henri Moissan.—Already inserted.

Hydrobromic Reaction of the Copper Salts.—G. Denigés.—The author maintains that the procedure given by P. Sabatier for the detection of traces of cupric salts (*Bull. Soc. Chim.*, July 20, 1894, p. 683) is substantially identical with that which he made known in 1889 (*Comptes Rendus*, cviii., p. 568; and *Soc. de Pharmacie de Bordeaux*, March and April, 1889).

Novel Series of Colouring Matters.—C. Friedel.—The author obtains a violet-red and an orange colouring matter from the product formed on heating to 120° in the oil-bath a mixture of 30 grms. methylacetanilide and 18 grms. phosphorus oxychloride until a considerable quantity of hydrochloric acid has escaped. The product dissolves in water with a yellowish brown colour. If the liquid is heated and treated with sodium carbonate, as long as effervescence is produced it takes a magenta-red and gives a precipitate of the same colour, which may be obtained by the process of "salting out."

Reduction of Nitro-aromatic Derivatives in a Neutral Liquid, and the Formation of Aromatic Hydroxylamines.—Lumière Bros. and Seyewitz.—The process of the reduction of mononitro-aromatic derivatives in a neutral liquid by zinc-powder and water in presence of calcium chlorides enables us to obtain the corresponding hydroxylamines when there do not occur in the nucleus any hydroxylic or amidic substitutions. In the latter case we obtain the total product of reduction, amido-phenol or diamine, in a very pure state, and with a good yield.

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.

Bronzing Copper Black.—I should be much obliged for information as to the method of bronzing copper black. It is done, I believe, by the agency of silver and copper nitrate applied to the article to be bronzed.—A. C.

MEETINGS FOR THE WEEK.

Monday, 28th.—Society of Arts, 8. (Cantor Lectures). "The Arc Light," by Prof. Silvanus P. Thompson, F.R.S.
— Medical, 8.30.
Tuesday, 29th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
Wednesday, 30th.—Society of Arts, 8. "Peking," by Thos. Child.
— British Astronomical Association, 5.
Thursday, 31st.—Royal, 4 30. "New Gaseous Constituent of the Atmosphere," by Lord Rayleigh and Prof. Ramsay, F.R.S., with Description of its Spectrum by W. Crookes, F.R.S. Discussion follows.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Four English Humourists of the Nineteenth Century," by W. S. Lilly, M.A.
— Society of Arts, 4.30. "India and its Women," by S. E. J. Clarke. (At Imperial Institute).
Friday, Feb. 1st.—Royal Institution, 9. "Acting—An Art," by Henry Irving.
— Geologists' Association, 8. (Anniversary).
— Quekett Club, 8.
Saturday, 2nd.—Royal Institution, 3. "Stained Glass Windows and Painted Glass," by Lewis F. Day.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1836.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

Thursday, January 31st, 1895.

The Lord Kelvin, D.C.L., LL.D., President, in the Chair.

The following papers were read:—

"*Argon: a New Constituent of the Atmosphere.*" By Lord Rayleigh, Sec. R.S., and William Ramsay, F.R.S., Professor of Chemistry, University College, London. (Abstract).

I.—*Density of Nitrogen from Various Sources.*

In a former paper[*] it has been shown that nitrogen extracted from chemical compounds is about ½ per cent lighter than "atmospheric nitrogen."

The mean numbers for the weights of gas contained in the globe used were as follows:—

From nitric oxide	2·3001
From nitrous oxide	2·2990
From ammonium nitrite	2·2987

while for "atmospheric nitrogen" there was found—

By hot copper, 1892..	2·3103
By hot iron, 1893	2·3100
By ferrous hydrate, 1894.. ..	2·3102

At the suggestion of Professor Thorpe experiments were subsequently tried with nitrogen liberated from *urea* by the action of sodium hypobromite. The hypobromite was prepared from commercial materials in the proportions recommended for the analysis of urea. The reaction was well under control, and the gas could be liberated as slowly as desired.

In the first experiment the gas was submitted to no other treatment than slow passage through potash and phosphoric anhydride, but it soon became apparent that the nitrogen was contaminated. The "inert and inodorous" gas attacked vigorously the mercury of the Töpler pump, and was described as smelling like a dead rat. As to the weight, it proved to be in excess even of the weight of atmospheric nitrogen.

The corrosion of the mercury and the evil smell were in great degree obviated by passing the gas over hot metals. For the fillings of June 6, 9, and 13 the gas passed through a short length of tube containing copper in the form of fine wire heated by a flat Bunsen burner, then through the furnace over red-hot iron, and back over copper oxide. On June 19 the furnace tubes were omitted, the gas being treated with the red-hot copper only. The mean result, reduced so as to correspond with those above quoted, is 2·2985.

Without using heat, it has not been found possible to prevent the corrosion of the mercury. Even when no urea is employed, and air, simply bubbled through the hypobromite solution, is allowed to pass with constant shaking over mercury contained in a U-tube, the surface of the metal was soon fouled.

Although the results relating to urea nitrogen are interesting for comparison with that obtained from other nitrogen compounds, the original object was not attained on account of the necessity of retaining the treatment with hot metals. We have found, however, that nitrogen from ammonium nitrite may be prepared without the employment of hot tubes whose weight agrees with that above quoted. It is true that the gas smells slightly of ammonia, easily removable by sulphuric acid, and apparently also of oxides of nitrogen. The mean result from three fillings is 2·2987.

It will be seen that, in spite of the slight nitrous smell, there is no appreciable difference in the densities of gas prepared from ammonium nitrite with and without the treatment by hot metals. The result is interesting as showing that the agreement of numbers obtained for chemical nitrogen does not depend upon the use of a red heat in the process of purification.

The five results obtained in more or less distinct ways for chemical nitrogen stand thus:—

From nitric oxide	2·3001
From nitrous oxide	2·2990
From ammonium nitrite purified at a red heat	2·2987
From urea	2·2985
From ammonium nitrite purified in the cold	2·2987
Mean..	2·2990

These numbers as well as those above quoted for "atmospheric nitrogen," are subject to a deduction of 0·0006 for the shrinkage of the globe when exhausted.[*] If they are then multiplied in the ratio of 2·3108 : 1·2572, they will express the weights of the gas in grms. per litre. Thus, as regards the mean numbers, we find as the weight per litre under standard conditions of chemical nitrogen 1·2505, that of atmospheric nitrogen being 1·2572.

It is of interest to compare the density of nitrogen obtained from chemical compounds with that of oxygen. We have $N_2 : O_2 = 2{\cdot}2984 : 2{\cdot}6276 = 0{\cdot}87471$; so that if $O_2 = 16$, $N_2 = 13{\cdot}9954$. Thus, when the comparison is with chemical nitrogen, the ratio is very nearly that of 16 : 14; but if "atmospheric nitrogen" be substituted, the ratio of small integers is widely departed from.

To the above list may be added nitrogen prepared in yet another manner, whose weight has been determined subsequently to the isolation of the new dense constituent of the atmosphere. In this case nitrogen was actually extracted from air by means of magnesium. The nitrogen thus separated was then converted into ammonia by action of water upon the magnesium nitride and afterwards liberated in the free state by means of calcium hypochlorite. The purification was conducted in the usual way, and included passage over red-hot copper and copper oxide. The following was the result:—

Globe empty, Oct. 30, Nov. 5..	2·82313
Globe full, Oct. 31	0·52395
Weight of gas.. ..	2·29918

It differs inappreciably from the mean of other results, viz., 2·2990, and is of special interest as relating to gas which at one stage of its history formed part of the atmosphere.

Another determination, with a different apparatus, of the density of "chemical" nitrogen from the same source, magnesium nitride, which had been prepared by passing "atmospheric" nitrogen over ignited magnesium, may here be recorded. The sample differed from that previously mentioned, inasmuch as it had not been subjected to treatment with red-hot copper. After treating the nitride with water, the resulting ammonia was distilled off, and collected in hydrochloric acid; the solution was evaporated by degrees, the dry ammonium chloride was dissolved in water, and its concentrated solution added to a freshly-prepared solution of sodium hypobromite.

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[*] Rayleigh, "On an Anomaly encountered in Determinations of the Density of Nitrogen Gas," *Roy. Soc. Proc.*, vol. lv., p. 340, 1894.

[*] Rayleigh, "On the Densities of the Principal Gases," *Roy. Soc. Proc.*, vol. liii., p. 134, 1893.

The nitrogen was collected in a gas-holder over water which had previously been boiled, so as, at all events partially, to expel air. The nitrogen passed into the vacuous globe through a solution of potassium hydroxide, and through two drying-tubes, one containing soda-lime, and the other phosphoric anhydride.

At 18·38° C. and 754·4 m.m. pressure, 162·843 c.c. of this nitrogen weighed 0·18963 grm. Hence,

Weight of 1 litre at 0° C. and 760 m.m. pressure = 1·2521 grm.

The mean result of the weight of 1 litre of "chemical" nitrogen has been found to equal 1·2505. It is therefore seen that "chemical" nitrogen, derived from "atmospheric" nitrogen, without any exposure to red-hot copper, possesses the usual density.

Experiments were also made, which had for their object to prove that the ammonia produced from the magnesium nitride is identical with ordinary ammonia, and contains no other compound of a basic character. For this purpose the ammonia was converted into ammonium chloride, and the percentage of chlorine determined by titration with a solution of silver nitrate which had been standardised by titrating a specimen of pure sublimed ammonium chloride. The silver solution was of such a strength that 1 c.c. precipitated the chlorine from 0·001701 grm. of ammonium chloride.

1. Ammonium chloride from orange-coloured sample of magnesium nitride contained 66·35 per cent of chlorine.
2. Ammonium chloride from blackish magnesium nitride contained 66·35 per cent of chlorine.
3. Ammonium chloride from nitride containing a large amount of unattacked magnesium contained 66·30 per cent of chlorine.

Taking for the atomic weights of hydrogen H = 1·0032, of nitrogen N = 14·04, and of chlorine Cl = 35·46, the theoretical amount of chlorine in ammonium chloride is 66·27 per cent.

From these results—that nitrogen prepared from magnesium nitride, obtained by passing "atmospheric" nitrogen over red-hot magnesium, has the density of "chemical" nitrogen, and that ammonium chloride, prepared from magnesium nitride, contains practically the same percentage of chlorine as pure ammonium chloride—it may be concluded that red-hot magnesium withdraws from "atmospheric nitrogen" no substance other than nitrogen capable of forming a basic compound with hydrogen.

II.—*Reasons for Suspecting a Hitherto Undiscovered Constituent in Air.*

When the discrepancy of weights was first encountered, attempts were naturally made to explain it by contamination with known impurities. Of these the most likely appeared to be hydrogen, present in the lighter gas in spite of the passage over red-hot cupric oxide. But inasmuch as the intentional introduction of hydrogen into the heavier gas, afterwards treated in the same way with cupric oxide, had no effect upon its weight, this explanation had to be abandoned, and finally it became clear that the difference could not be accounted for by the presence of any known impurity. At this stage it seemed not improbable that the lightness of the gas extracted from chemical compounds was to be explained by partial dissociation of nitrogen molecules N_2 into detached atoms. In order to test this suggestion both kinds of gas were submitted to the action of the silent electric discharge, with the result that both retained their weights unaltered. This was discouraging, and a further experiment pointed still more markedly in the negative direction. The chemical behaviour of nitrogen is such as to suggest that dissociated atoms would possess a high degree of activity, and that even though they might be formed in the first instance, their life would probably be short. On standing they might be expected to disappear, in partial analogy with the known behaviour of ozone. With this idea in view, a sample of chemically prepared nitrogen was stored for eight months. But at the end of this time the density showed no sign of increase, remaining exactly as at first.[*]

Regarding it as established that one or other of the gases must be a mixture, containing, as the case might be, an ingredient much heavier or much lighter than ordinary nitrogen, we had to consider the relative probabilities of the various possible interpretations. Except upon the already discredited hypothesis of dissociation, it was difficult to see how the gas of chemical origin could be a mixture. To suppose this would be to admit two kinds of nitric acid, hardly reconcilable with the work of Stas and others upon the atomic weight of that substance. The simplest explanation in many respects was to admit the existence of a second ingredient in air from which oxygen, moisture, and carbonic anhydride had already been removed. The proportional amount required was not great. If the density of the supposed gas were double that of nitrogen, one-half per cent only by volume would be needed; or if the density were but half as much again as that of nitrogen, then 1 per cent would still suffice. But in accepting this explanation, even provisionally, we had to face the improbability that a gas surrounding us on all sides, and present in enormous quantities, could have remained so long unsuspected.

The method of most universal application by which to test whether a gas is pure or a mixture of components of different densities is that of diffusion. By this means Graham succeeded in effecting a partial separation of the nitrogen and oxygen of the air, in spite of the comparatively small difference of densities. If the atmosphere contain an unknown gas of anything like the density supposed, it should be possible to prove the fact by operations conducted upon air which had undergone atmolysis. This experiment, although in view from the first, was not executed until a later stage of the inquiry (§ 6), when results were obtained sufficient of themselves to prove that the atmosphere contains a previously unknown gas.

But although the method of diffusion was capable of deciding the main, or at any rate the first question, it held out no prospect of isolating the new constituent of the atmosphere, and we therefore turned our attention in the first instance to the consideration of methods more strictly chemical. And here the question forced itself upon us as to what really was the evidence in favour of the prevalent doctrine that the inert residue from air after withdrawal of oxygen, water, and carbonic anhydride, is all of one kind.

The identification of "phlogisticated air" with the constituent of nitric acid is due to Cavendish, whose method consisted in operating with electric sparks upon a short column of gas confined with potash over mercury at the upper end of an inverted U-tube.[†]

Attempts to repeat Cavendish's experiment in Cavendish's manner have only increased the admiration with which we regard this wonderful investigation. Working on almost microscopical quantities of material, and by operations extending over days and weeks, he thus established one of the most important facts in chemistry. And what is still more to the purpose, he raises as distinctly as we could do, and to a certain extent resolves, the question above suggested. The passage is so important that it will be desirable to quote it at full length.

"As far as the experiments hitherto published extend, we scarcely know more of the phlogisticated part of our atmosphere than that it is not diminished by lime-water, caustic alkalis, or nitrous air; that it is unfit to support fire or maintain life in animals; and that its specific gravity is not much less than that of common air: so that though the nitrous acid, by being united to phlogiston, is converted into air possessed of these properties,

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[*] *Roy. Soc. Proc.*, lv., p. 344, 1894.

[†] "Experiments on Air," *Phil. Trans.*, lxxv., p. 372, 1785.

and consequently, though it was reasonable to suppose that part at least of the phlogisticated air of the atmosphere consists of this acid united to phlogiston, yet it was fairly to be doubted whether the whole is of this kind, or whether there are not in reality many different substances compounded together by us under the name of phlogisticated air. I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid, or whether there was not a part of a different nature to the rest, which would refuse to undergo that change. The foregoing experiments indeed in some measure decided this point, as much the greatest part of the air let up into the tube lost its elasticity; yet as some remained unabsorbed it did not appear for certain whether that was of the same nature as the rest or not. For this purpose I diminished a similar mixture of dephlogisticated and common air, in the same manner as before, till it was reduced to a small part of its original bulk. I then, in order to decompound as much as I could of the phlogisticated air which remained in the tube, added some dephlogisticated air to it, and continued the spark until no further diminution took place. Having by these means condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulphur to absorb the dephlogisticated air; after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated air let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$th part of the whole."

Although Cavendish was satisfied with his result, and does not decide whether the small residue was genuine, our experiments about to be related render it not improbable that his residue was really of a different kind from the main bulk of the "phlogisticated air," and contained the gas now called argon.

Cavendish gives data* from which it is possible to determine the rate of absorption of the mixed gases in his experiment. This was about 1 c.c. per hour, of which two-fifths would be nitrogen.

III.—*Methods of Causing Free Nitrogen to Combine.*

To eliminate nitrogen from air, in order to ascertain whether any other gas could be detected, involves the use of some absorbent. The elements which have been found to combine directly with nitrogen are: boron, silicon, titanium, lithium, strontium, barium, magnesium, aluminium, mercury, and, under the influence of an electric discharge, hydrogen in presence of acid, and oxygen in presence of alkali. Besides these, a mixture of barium carbonate and carbon at a high temperature is known to be effective. Of those tried, magnesium in the form of turnings was found to be the best. When nitrogen is passed over magnesium, heated in a tube of hard glass to bright redness, combustion with incandescence begins at the end of the tube through which the gas is introduced, and proceeds regularly until all the metal has been converted into nitride. Between 7 and 8 litres of nitrogen can be absorbed in a single tube; the nitride formed is a porous, dirty orange-coloured substance.

IV.—*Early Experiments on Sparking Nitrogen with Oxygen in Presence of Alkali.*

In our earliest attempts to isolate the suspected gas by the method of Cavendish, we used a Ruhmkorff coil of medium size actuated by a battery of five Grove cells. The gases were contained in a test-tube standing over a large quantity of weak alkali, and the current was conveyed in wires insulated by U-shaped glass tubes passing through the liquid round the mouth of the test-tube. With the given battery and coil a somewhat short spark or arc of about 5 m.m. was found to be more favourable than a longer one. When the mixed gases were in the right proportion the rate of absorption was about 30 c.c. per hour, or thirty times as fast as Cavendish could work with the electrical machine of his day.

To take an example, one experiment of this kind started with 50 c.c. of air. To this oxygen was gradually added until, oxygen being in excess, there was no perceptible contraction during an hour's sparking. The remaining gas was then transferred at the pneumatic trough to a small measuring vessel, sealed by mercury, in which the volume was found to be 1·0 c.c. On treatment with alkaline pyrogallate the gas shrank to 0·32 c.c. That this small residue could not be nitrogen was argued from the fact that it had withstood the prolonged action of the spark, although mixed with oxygen in nearly the most favourable proportion.

The residue was then transferred to the test-tube with an addition of another 50 c.c. of air, and the whole worked up with oxygen as before. The residue was now 2·2 c.c., and, after removal of oxygen, 0·76 c.c.

Although it seemed almost impossible that these residues could be either nitrogen or hydrogen, some anxiety was not unnatural, seeing that the final sparking took place under somewhat abnormal conditions. The space was very restricted, and the temperature (and with it the proportion of aqueous vapour) was unduly high. But any doubts that were felt upon this score were removed by comparison experiments in which the whole quantity of air operated on was very small. Thus, when a mixture of 5 c.c. of air with 7 c.c. of oxygen was sparked for 1¼ hours, the residue was 0·47 c.c., and after removal of oxygen 0·06 c.c. Several repetitions having given similar results, it became clear that the final residue did not depend upon anything that might happen when sparks passed through a greatly reduced volume, *but was in proportion to the amount of air operated upon.*

No satisfactory examination of the residue which refused to be oxidised could be made without the accumulation of a larger quantity. This, however, was difficult of attainment at the time in question. It was thought that the cause probably lay in the solubility of the gas in water, a suspicion since confirmed. At length, however, a sufficiency was collected to allow of sparking in a specially constructed tube, when a comparison with the air spectrum, taken under similar conditions, proved that, at any rate, the gas was not nitrogen. At first scarcely a trace of the principal nitrogen lines could be seen, but after standing over water for an hour or two these lines became apparent.

V.—*Early Experiments on Withdrawal of Nitrogen from Air by means of Red-hot Magnesium.*

A preliminary experiment carried out by Mr. Percy Williams on the absorption of atmospheric nitrogen, freed from oxygen by means of red-hot copper, in which the gas was not passed over, but simply allowed to remain in contact with the metal, gave a residue of density 14·88. This result, although not conclusive, was encouraging; and an attempt was made, on a larger scale, by passing atmospheric nitrogen backwards and forwards over red-hot magnesium from one large gas-holder to another to obtain a considerable quantity of the heavier gas. In the course of ten days about 1500 c.c. were collected and transferred gradually to a mercury gas-holder, from which the gas was passed over soda-lime, phosphoric anhydride, magnesium at a red heat, copper oxide, soda-lime, and phosphoric anhydride into a second mercury gas-holder. After some days the gas was reduced in volume to about 200 c.c., and its density was found to be 16·1. After further absorption, in which the volume was still further reduced, the density of the residue was increased to 19·09.

On passing sparks for several hours through a mixture of a small quantity of this gas with oxygen, its volume was still further reduced. Assuming that this reduction

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* *Phil. Trans.*, lxxviii., p. 271, 1788.

was due to the further elimination of nitrogen, the density of the remaining gas was calculated to be 20·0.

The spectrum of the gas of density 19·09, though showing nitrogen bands, showed many other lines which were not recognisable as belonging to any known element.

VI.—*Proof of the Presence of Argon in Air by means of Atmolysis.*

It has already (§ 2) been suggested that if "atmospheric nitrogen" contains two gases of different densities, it should be possible to obtain direct evidence of the fact by the method of atmolysis. The present section contains an account of carefully conducted experiments directed to this end.

The atmolyser was prepared (after Graham) by combining a number of "churchwarden" tobacco pipes. At first twelve pipes were used in three groups, each group including four pipes connected in series. The three groups were then connected in parallel, and placed in a large glass tube closed in such a way that a partial vacuum could be maintained in the space outside the pipes by a water pump. One end of the combination of pipes was open to the atmosphere; the other end was connected to a bottle aspirator, initially full of water, and so arranged as to draw about 2 per cent of the air which entered the other end of the pipes. The gas collected was thus a very small proportion of that which leaked through the pores of the pipes, and should be relatively rich in the heavier constituents of the atmosphere. The flow of water from the aspirator could not be maintained very constant, but the rate of 2 per cent was never much exceeded.

The air thus obtained was treated exactly as ordinary air had been treated in determinations of the density of atmospheric nitrogen. Oxygen was removed by red-hot copper, followed by cupric oxide, ammonia by sulphuric acid, moisture and carbonic acid by potash and phosphoric anhydride.

In a total weight of approximately 2·3 grms. the excess of weight of the diffused nitrogen over ordinary atmospheric nitrogen was in four experiments, 0·0049, 0·0014, 0·0027, 0·0015.

The mean excess of the four determinations is 0·00262 grm., or, if we omit the first, which depended upon a vacuum weighing of two months old, 0·00187 grm.

The gas from prepared air was thus in every case denser than from unprepared air, and to an extent much beyond the possible errors of experiment. The excess was, however, less than had been expected, and it was thought that the arrangement of the pipes could be improved. The final delivery of gas from each of the groups in parallel being so small in comparison with the whole streams concerned, it seemed possible that each group was not contributing its proper share, and even that there might be a flow in the wrong direction at the delivery end of one or two of them. To meet this objection, the arrangement in parallel had to be abandoned, and for the remaining experiments eight pipes were connected in simple series. The porous surface in operation was thus reduced, but this was partly compensated for by an improved vacuum. Two experiments were made under the new conditions, in which the excess was I., 0·0037; II., 0·0033.

The excess being larger than before is doubtless due to the greater efficiency of the atmolysing apparatus. It should be mentioned that the above recorded experiments include all that have been tried, and the conclusion seems inevitable that "atmospheric nitrogen" is a mixture, and not a simple body.

It was hoped that the concentration of the heavier constituent would be sufficient to facilitate its preparation in a pure state by the use of prepared air in substitution for ordinary air in the oxygen apparatus. The advance of 3½ m.m. on the 11 m.m., by which atmospheric nitrogen is heavier than chemical nitrogen, is indeed not to be despised, and the use of prepared air would be convenient if the diffusion apparatus could be set up on a large scale and be made thoroughly self-acting.

VII.—*Negative Experiments to prove that Argon is not derived from Nitrogen from Chemical Sources.*

Although the evidence of the existence of argon in the atmosphere, derived from the comparison of densities of atmospheric and chemical nitrogen and from the diffusion experiments (§ VI.), appeared overwhelming, we have thought it undesirable to shrink from any labour that would tend to complete the verification. With this object in view, an experiment was undertaken and carried to a conclusion on November 13, in which 3 litres of chemical nitrogen, prepared from ammonium nitrite, were treated with oxygen in precisely the manner in which atmospheric nitrogen had been found to yield a residue of argon. The gas remaining at the close of the large scale operation was worked up as usual with battery and coil until the spectrum showed only slight traces of the nitrogen lines. When cold, the residue measured 4 c.c. This was transferred, and after treatment with alkaline pyrogallate to remove oxygen measured 3·3 c.c. If atmospheric nitrogen had been employed, the final residue should have been about 30 c.c. Of the 3·3 c.c. actually left, a part is accounted for by an accident, and the result of the experiment is to show that argon is not formed by sparking a mixture of oxygen and chemical nitrogen.

In a second experiment of the same kind 5660 c.c. of nitrogen from ammonium nitrite was treated with oxygen. The final residue was 3·5 c.c. and was found to consist mainly of argon.

The source of the residual argon is to be sought in the water used for the manipulation of the large quantities of gas (6 litres of nitrogen and 11 litres of oxygen) employed. When carbonic acid was collected in a similar manner and subsequently absorbed by potash, it was found to have acquired a contamination consistent with this explanation.

Negative experiments were also carried out, absorbing nitrogen by means of magnesium. In one instance 3 litres of nitrogen prepared from ammonium chloride and bleaching-powder was reduced in volume to 4·5 c.c., and on sparking with oxygen its volume was further reduced to about 3 c.c. The residue appeared to consist of argon. Another experiment, in which 15 litres of nitrogen from ammonium nitrite was absorbed, gave a final residue of 3·5 c.c. Atmospheric nitrogen, in the latter case, would have yielded 150 c.c., hence less than $\frac{1}{40}$th of the normal quantity was obtained. It should be mentioned that leakage occurred at one stage, by which perhaps 200 c.c. of air entered the apparatus; and, besides, the nitrogen was collected over water from which it doubtless acquired some argon. Quantitative negative experiments of this nature are exceedingly difficult, and require a long time to carry them to a successful conclusion.

VIII.—*Separation of Argon on a Large Scale.*

To prepare argon on a large scale, air is freed from oxygen by means of red-hot copper. The residue is then passed from a gas-holder through a combustion tube, heated in a furnace, and containing copper, in order to remove all traces of oxygen; the issuing gas is then dried by passage over soda-lime and phosphorus pentoxide, after passage through a small U-tube containing sulphuric acid, to indicate the rate of flow. It then enters a combustion-tube packed tightly with magnesium turnings, and heated to redness in a second furnace. From this tube it passes through a second index-tube, and enters a small gas-holder capable of containing 3 or 4 litres. A single tube of magnesium will absorb from 7 to 8 litres of nitrogen. The temperature must be nearly that of the fusion of the glass, and the current of gas must be carefully regulated, else the heat developed by the union of the magnesium with nitrogen will fuse the tube.

Having collected the residue from 100 or 150 litres of atmospheric nitrogen, which may amount to 4 or 5 litres, it is transferred to a small gas-holder connected with an apparatus, whereby, by means of a species of a self-acting Sprengel's pump, the gas is caused to circulate through a tube half filled with copper and half with copper oxide; it then traverses a tube half filled with soda-lime and half with phosphorus pentoxide; it then passes a reservoir of about 300 c.c. capacity, from which, by raising a mercury reservoir, it can be expelled into a small gas-holder. Next it passes through a tube containing magnesium turnings heated to bright redness. The gas is thus freed from any possible contamination with oxygen, hydrogen, or hydrocarbons, and nitrogen is gradually absorbed. As the amount of gas in the tubes and reservoir diminishes in volume, it draws supplies from the gas-holder, and, finally, the circulating system is full of argon in a pure state. The circulating system of tubes is connected with a mercury pump, so that, in changing the magnesium tube, no gas may be lost. Before ceasing to heat the magnesium tube the system is pumped empty, and the collected gas is restored to the gas-holder; finally, all the argon is transferred from the mercury reservoir to the second small gas-holder, which should preferably be filled with water saturated with argon, so as to prevent contamination from oxygen or nitrogen; or, if preferred, a mercury gas-holder may be employed. The complete removal of nitrogen from argon is very slow towards the end, but circulation for a couple of days usually effects it.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation. In extending the scale we had the great advantage of the advice of Mr. Crookes, who not long since called attention to the flame rising from platinum terminals, which convey a high tension alternating electric discharge, and pointed out its dependence upon combustion of the nitrogen and oxygen of the air.* The plant consists of a De Meritens alternator, actuated by a gas engine, and the currents are transformed to a high potential by means of a Ruhmkorff or other suitable induction coil. The highest rate of absorption of the mixed gases yet attained is 3 litres per hour, about 3000 times that of Cavendish. It is necessary to keep the apparatus cool, and from this and other causes a good many difficulties have been encountered.

In one experiment of this kind, the total air led in after seven days' working, amounted to 7925 c.c., and of oxygen (prepared from chlorate of potash), 9137 c.c. On the eighth and ninth days oxygen alone was added, of which about 500 c.c. was consumed, while there remained about 700 c.c. in the flask. Hence the proportion in which the air and oxygen combined was as 79 : 96. The progress of the removal of the nitrogen was examined from time to time with the spectroscope, and became ultimately very slow. At last the yellow line disappeared, the contraction having apparently stopped for two hours. It is worthy of notice that with the removal of the nitrogen, the arc discharge changes greatly in appearance, becoming narrower and blue rather than greenish in colour.

The final treatment of the residual 700 c.c. of gas was on the model of the small scale operations already described. Oxygen or hydrogen could be supplied at pleasure from an electrolytic apparatus, but in no way could the volume be reduced below 65 c.c. This residue refused oxidation, and showed no trace of the yellow line of nitrogen, even under favourable conditions.

When the gas stood for some days over water, the nitrogen line reasserted itself in the spectrum, and many hour's sparking with a little oxygen was required again to get rid of it. Intentional additions of air to gas free from nitrogen showed that about 1½ per cent was clearly, and about 3 per cent was conspicuously, visible. About the same numbers apply to the visibility of nitrogen in oxygen when sparked under these conditions, that is, at atmospheric pressure, and with a jar connected to the secondary terminals.

IX.—*Density of Argon prepared by means of Oxygen.*

A first estimate of the density of argon prepared by the oxygen method was founded upon the data already recorded respecting the volume present in air, on the assumption that the accurately known densities of atmospheric and of chemical nitrogen differ on account of the presence of argon in the former, and that during the treatment with oxygen nothing is oxidised except nitrogen. Thus, if—

D = density of chemical nitrogen,
D' = ,, atmospheric nitrogen,
d = ,, argon,
α = proportional volume of argon in atmospheric nitrogen,

the law of mixtures give—

$$\alpha d+(1-\alpha)D=D',$$

or—

$$d=D+(D'-D)/\alpha.$$

In this formula $D'-D$ and α are both small, but they are known with fair accuracy. From the data already given—

$$\alpha=\frac{65}{0{\cdot}79\times7925},$$

whence if (on an arbitrary scale of reckoning) $D=2{\cdot}2990$, $D'=2{\cdot}3102$, we find $d=3{\cdot}378$. Thus if N_2 be 14, or O_2 be 16, the density of argon is 20·6.

A direct determination by weighing is desirable, but hitherto it has not been feasible to collect by this means sufficient to fill the large globe employed for other gases. A *mixture* of about 400 c.c. of argon with pure oxygen, however, gave the weight 2·7315, 0·1045 in excess of the weight of oxygen, viz., 2·6270. Thus, if α be the ratio of the volume of argon to the whole volume, the number for argon will be—

$$2{\cdot}6270+0{\cdot}1045/\alpha.$$

The value of α, being involved only in the excess of weight above that of oxygen, does not require to be known very accurately. Sufficiently concordant analyses by two methods gave $\alpha=0{\cdot}1845$; whence for the weight of the gas we get 3·193, so that, if $O_2=16$, the density of the gas would be 19·45. An allowance for residual nitrogen, still visible in the gas before admixture of oxygen, raises this number to 19·7, which may be taken as the density of pure argon resulting from this determination.

X.—*Density of Argon prepared by means of Magnesium.*

The density of the original sample of argon prepared has already been mentioned. It was 19·09; and, after sparking with oxygen, it was calculated to be 20·0. The most reliable results of a number of determinations give it as 19·90. The difficulty in accurately determining the density is to make sure that all nitrogen has been removed. The sample of density 19·90 showed no spectrum of nitrogen when examined in a vacuum tube. It is right, however, to remark that the highest density registered was 20·38. But there is some reason here to distrust the weighing of the vacuous globe.

XI.—*Spectrum of Argon.*

The spectrum of argon, seen in a vacuum tube of about 3 m.m. pressure, consists of a great number of lines, distributed over almost the whole visible field. Two lines are specially characteristic; they are less refrangible than the red lines of hydrogen or lithium, and serve well to identify the gas, when examined in this way. Mr. Crookes, who will give a full account of the spectrum in a separate communication, has kindly furnished us with the accurate wave-lengths of these lines, as well as of some others next to be described; they are respectively 696·56 and 705·64, 10^{-8} m.m.

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* Chemical News, lxv., p. 301, 1892.

Besides these red lines, a bright yellow line, more refrangible than the sodium line, occurs at 603·84. A group of five bright green lines occurs next, besides a number of less intensity. Of the group of five, the second, which is perhaps the most brilliant, has the wave-length 561·00. There is next a blue or blue violet line of wave-length 470·2; and last, in the less easily visible part of the spectrum, there are five strong violet lines, of which the fourth, which is the most brilliant, has the wave-length 420·0.

Unfortunately, the red lines, which are not to be mistaken for those of any other substance, are not easily seen when a jar discharge is passed through argon at atmospheric pressure. The spectrum seen under these conditions has been examined by Professor Schuster. The most characteristic lines are perhaps those in the neighbourhood of F, and are very easily seen if there be not too much nitrogen, in spite of the presence of some oxygen and water vapour. The approximate wave-lengths are—

487·91..	Strong.
[486·07]	F.
484·71..	Not quite so strong.
480·52..	Strong.
476·50..	Fairly strong characteristic triplet.
473·53..	
472·56..	

It is necessary to anticipate Mr. Crookes's communication, and to state that when the current is passed from the induction coil in one direction, that end of the capillary tube next the positive pole appears of a redder, and that next the negative pole of a bluer hue. There are, in effect, two spectra, which Mr. Crookes has succeeded in separating to a considerable extent. Mr. E. C. Baly,* who has noticed a similar phenomenon, attributes it to the presence of two gases. He says:—"When an electric current is passed through a mixture of two gases, one is separated from the other and appears in the negative glow." The conclusion would follow that what we have termed "argon" is in reality a mixture of two gases which have as yet not been separated. This conclusion, if true, is of great importance, and experiments are now in progress to test it by the use of other physical methods. The full bearing of this possibility will appear later.

The presence of a small quantity of nitrogen interferes greatly with the argon spectrum. But we have found that in a tube with platinum electrodes, after the discharge has been passed for four hours, the spectrum of nitrogen disappears, and the argon spectrum manifests itself in full purity. A specially constructed tube with magnesium electrodes, which we hoped would yield good results, removed all traces of nitrogen, it is true; but hydrogen was evolved from the magnesium, and showed its characteristic lines very strongly. However, these are easily identified. The gas evolved on heating magnesium *in vacuo*, as proved by a separate experiment, consists entirely of hydrogen.

Mr. Crookes has proved the identity of the chief lines of the spectrum of gas separated from air-nitrogen by aid of magnesium with that remaining after sparking the air-nitrogen with oxygen in presence of caustic soda solution.

Professor Schuster has also found the principal lines identical in the spectra of the two gases, as observed by the jar discharge at atmospheric pressure.

XII.—*Solubility of Argon in Water.*

Determinations of the solubility in water of argon prepared by sparking, gave 3·94 volumes per 100 of water at 12°. The solubility of gas prepared by means of magnesium was found to be 4·05 volumes per 100 at 13·9°. The gas is therefore about 2½ times as soluble as nitrogen, and possesses approximately the same solubility as oxygen.

The fact that argon is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain-water. Experiment has confirmed this anticipation. "Nitrogen" prepared from the dissolved gases of water supplied from a rain-water cistern was weighed upon two occasions. The weights, corresponding to those recorded in § I., were 2·3221 and 2·3227, showing an excess of 24 m.grms. above the weight of true nitrogen. Since the corresponding excess for "atmospheric nitrogen" is 11 m.grms. we conclude that the water "nitrogen" is relatively more than twice as rich in argon.

On the other hand, gas evolved from the hot spring at Bath, and collected for us by Dr. A. Richardson, gave a residue after removal of oxygen and carbonic acid, whose weight was only about midway between that of true and atmospheric nitrogen.

XIII.—*Behaviour at Low Temperatures.**

Preliminary experiments, carried out to liquefy argon at a pressure of about 100 atmospheres, and at a temperature of −90°, failed. No appearance of liquefaction could be observed.

Professor Charles Olszewski, of Cracow, the well-known authority on the constants of liquefied gases at low temperatures, kindly offered to make experiments on the liquefaction of argon. His results are embodied in a separate communication, but it is allowable to state here that the gas has a lower critical point and a lower boiling point than oxygen, and that he has succeeded in solidifying argon to white crystals. The sample of gas he experimented with was exceptionally pure, and had been prepared by help of magnesium. It showed no trace of nitrogen when examined in a vacuum tube.

XIV.—*Ratio of Specific Heats.*

In order to decide regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. It will be remembered that, from the velocity of sound in a gas, the ratio of specific heat at constant pressure to that at constant volume can be deduced by means of the equation—

$$n\lambda = v = \sqrt{\left\{ \frac{e}{d}(1+\alpha t)\frac{C_p}{C_v} \right\}},$$

when n is the frequency, λ the wave-length of sound, v its velocity, e the isothermal elasticity, d the density, $(1+\alpha t)$ the temperature correction, C_p the specific heat at constant pressure, and C_v that at constant volume. In comparing two gases at the same temperature, each of which obeys Boyle's law with sufficient approximation, and in using the same sound, many of these terms disappear, and the ratio of specific heats of one gas may be deduced from that of the other, if known, by means of the proportion—

$$\lambda^2 d : \lambda'^2 d' :: 1{\cdot}41 : x,$$

where, for example, λ and d refer to air, of which the ratio is 1·41, according to observations by Röntgen, Wüllner, Kayser, and Jamin and Richard.

Two completely different series of observations, one in a tube of about 2 m.m. diameter, and one in one of 8 m.m., made with entirely different samples of gas, gave, the first, 1·65 as the ratio, and, the second, 1·61.

Experiments made with the first tube, to test the accuracy of its working, gave for carbon dioxide the ratio 1·276, instead of 1·288, the mean of all previous determinations; and the half wave-length of sound in hydrogen was found to be 73·6, instead of 74·5, the mean of those previously found. The ratio of the specific heats of hydrogen found was 1·39, instead of 1·402.

There can be no doubt, therefore, that argon gives practically the ratio of specific heats, viz., 1·66 proper to a gas in which all the energy is translational. The only

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* *Proc. Phys. Soc.*, 1893, p. 147.

* The arrangements for the experiments upon this branch of the subject were left entirely in Professor Ramsay's hands.

other gas which has been found to behave similarly is mercury gas, at a high temperature.*

XV.—*Attempts to induce Chemical Combination.*

Many attempts to induce argon to combine will be described in full in the complete paper. Suffice it to say here that all such attempts have as yet proved abortive. Argon does not combine with oxygen in presence of alkali under the influence of the electric discharge, nor with hydrogen in presence of acid or alkali also when sparked; nor with chlorine, dry or moist, when sparked; nor with phosphorus at a bright-red heat; nor with sulphur at bright redness. Tellurium may be distilled in a current of the gas; so may sodium and potassium, their metallic lustre remaining unchanged. It is unabsorbed by passing it over fused red-hot caustic soda, or soda-lime heated to bright redness; it passes unaffected over fused and bright red-hot potassium nitrate; and red-hot sodium peroxide does not combine with it. Persulphides of sodium and calcium are also without action at a red-heat. Platinum-black does not absorb it, nor does platinum sponge, and wet oxidising and chlorinating agents, such as nitro-hydrochloric acid, bromine water, bromine and alkali, and hydrochloric acid and potassium permanganate, are entirely without action. Experiments with fluorine are in contemplation, but the difficulty is great; and an attempt will be made to produce a carbon arc in the gas. Mixtures of sodium and silica and of sodium and boracic anhydride are also without action; hence it appears to resist attack by nascent silicon and by nascent boron.

XVI.—*General Conclusions.*

It remains, finally, to discuss the probable nature of the gas, or mixture of gases, which we have succeeded in separating from atmospheric air, and which we provisionally name *argon*.

The presence of argon in the atmosphere is proved by many lines of evidence. The high density of "atmospheric nitrogen," the lower density of nitrogen from chemical sources, and the uniformity in the density of samples of chemical nitrogen prepared from different compounds, lead to the conclusion that the cause of the anomaly is the presence of a heavy gas in air. If that gas possess the density 20 compared with hydrogen, "atmospheric" nitrogen should contain of it approximately 1 per cent. This is, in fact, found to be the case, Moreover, as nitrogen is removed from air by means of red-hot magnesium, the density of the remaining gas rises proportionately to the concentration of the heavier constituent.

Second.—This gas has been concentrated in the atmosphere by diffusion. It is true that it has not been freed from oxygen and nitrogen by diffusion, but the process of diffusion increases, relatively to nitrogen, the amount of argon in that portion which does not pass through the porous walls. This has been proved by its increase in density.

Third.—As the solubility of argon in water is relatively high, it is to be expected that the density of the mixture of argon and nitrogen, pumped out of water along with oxygen, should, after the removal of the oxygen, be higher than that of "atmospheric" nitrogen. Experiment has shown that the density is considerably increased.

Fourth.—It is in the highest degree improbable that two processes, so different from each other, should manufacture the same product. The explanation is simple if it be granted that these processes merely eliminate nitrogen from an "atmospheric" mixture. Moreover, as argon is an element, or a mixture of elements, its manufacture would mean its separation from one of the substances employed. The gas which can be removed from red-hot magnesium in a vacuum has been found to be wholly hydrogen. Nitrogen from chemical sources has been practically all absorbed by magnesium, and also when sparked in presence of oxygen; hence argon cannot have resulted from the decomposition of nitrogen. That it is not produced from oxygen is sufficiently borne out by its preparation by means of magnesium.

Other arguments could be adduced, but the above are sufficient to justify the conclusion that argon is present in the atmosphere.

The identity of the leading lines in the spectrum, the similar solubility and the similar density, appear to prove the identity of the argon prepared by both processes.

Argon is an element, or a mixture of elements, for Clausius has shown that if K be the energy of translatory motion of the molecules of a gas, and H their whole kinetic energy, then—

$$\frac{K}{H} = \frac{3(C_p - C_v)}{2C_v}$$

C_p and C_v denoting as usual the specific heat at constant pressure and at constant volume respectively. Hence if, as for mercury vapour and for argon (§ XIV.), the ratio of specific heats $C_p : C_v$ be $1\frac{2}{3}$, it follows that $K = H$, or that the whole kinetic energy of the gas is accounted for by the translatory motion of its molecules. In the case of mercury the absence of interatomic energy is regarded as proof of the monatomic character of the vapour, and the conclusion holds equally good for argon.

The only alternative is to suppose that if argon molecules are di- or polyatomic, the atoms acquire no relative motion, even of rotation, a conclusion exceedingly improbable in itself and one postulating the sphericity of such complex groups of atoms.

Now a monatomic gas can be only an element, or a mixture of elements; and hence it follows that argon is not of a compound nature.

From Avogadro's law, the density of a gas is half its molecular weight; and as the density of argon is approximately 20, hence its molecular weight must be 40. But its molecule is identical with its atom; hence its atomic weight, or, if it be a mixture, the mean of the atomic weights of that mixture, taken for the proportion in which they are present, must be 40.

There is evidence both for and against the hypothesis that argon is a mixture: for, owing to Mr. Crookes's observations of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well-known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture. The conclusions which follow are, however, so startling that in our future experimental work we shall endeavour to decide the question by other means.

For the present, however, the balance of evidence seems to point to simplicity. We have therefore to discuss the relations to other elements of an element of atomic weight 40. We inclined for long to the view that argon was possibly one or more than one of the elements which might be expected to follow fluorine in the periodic classification of the elements—elements which should have an atomic weight between 19, that of fluorine, and 23, that of sodium. But this view is completely put out of court by the discovery of the monatomic nature of its molecules.

The series of elements possessing atomic weights near 40 are—

Chlorine	35·5
Potassium	39·1
Calcium	40·0
Scandium	44·0

There can be no doubt that potassium, calcium, and

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* Kundt and Warburg, *Pog. Ann.*, cxxxv., pp. 337 and 527

scandium follow legitimately their predecessors in the vertical columns, lithium, beryllium, and boron, and that they are in almost certain relation with rubidium, strontium, and (but not so certainly) yttrium. If argon be a single element, then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which cannot be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements, they might find place in the eighth group, one after chlorine and one after bromine. Assuming 37 (the approximate mean between the atomic weights of chlorine and potassium) to be the atomic weight of the lighter element, and 40 the mean atomic weight found, and supposing that the second element has an atomic weight between those of bromine, 80, and rubidium, 85·5, viz., 82, the mixture should consist of 93·3 per cent of the lighter, and 6·7 per cent of the heavier element. But it appears improbable that such a high percentage as 6·7 of a heavier element should have escaped detection during liquefaction.

If it be supposed that argon belongs to the eighth group, then its properties would fit fairly well with what might be anticipated. For the series, which contains—

$$\mathrm{Si}_n^{\mathrm{IV.}},\ \mathrm{P}_4^{\mathrm{III.\ and\ V.}},\ \mathrm{S}_{8\ \mathrm{to}\ 2}^{\mathrm{II.\ to\ VI.}},\ \text{and}\ \mathrm{Cl}_2^{\mathrm{I.\ to\ VII.}},$$

might be expected to end with an element of monatomic molecules of no valency, *i.e.*, incapable of forming a compound, or if forming one, being an octad; and it would form a possible transition to potassium, with its monovalence, on the other hand. Such conceptions are, however, of a speculative nature; yet they may be perhaps excused, if they in any way lead to experiments which tend to throw more light on the anomalies of this curious element.

In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although a monatomic element, forms compounds which are by no means stable at a high temperature in the gaseous state; and attempts to produce compounds of argon may be likened to attempts to cause combination between mercury gas at 800° and other elements. As for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former and comparative molecular simplicity to the latter. Argon, with its comparatively low density and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered as a constituent of compound bodies.

We would suggest for this element, assuming provisionally that it is not a mixture, the symbol A.

We have to record our thanks to Messrs. Gordon, Kellas, and Matthews, who have materially assisted us in the prosecution of this research.

Mr. Crookes (before reading his paper) said—Allow me, Mr. President, to take this opportunity of striking the key-note of the chorus of applause and congratulations which will follow from all chemists present on this most valuable and important paper. The difficulties in a research of this kind are peculiar. Here we have a new chemical element, the principal properties of which seem to be the negation of all chemical properties. Chemists will understand how difficult it is to deal with anything which forms no compounds and unites with nothing. The discovery commenced by a prediction, followed after an interval by realisation. Discoveries of this kind are more important and take a higher rank, than discoveries which more or less come in a haphazard sort of way. The prediction and discovery of argon are only equalled by the few discoveries of elements which have been made in chemistry by the careful study of the periodic law, and to surpass it we must go back to the predicted existence and subsequent discovery of an unknown planet by Adams and Leverrier.

"*On the Spectra of Argon.*" By William Crookes, F.R.S., &c. (Abstract).

Through the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train.

Argon resembles nitrogen in that it gives two distinct spectra, according to the strength of the induction current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, the argon spectra both consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not at first show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and however free it was supposed to be from nitrogen, I could always detect the nitrogen bands in its spectrum. These, however, soon disappear when the induction spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum tubes best adapted for showing the spectra are of the ordinary Plücker form, having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is 3 m.m. At this point the colour of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wave-lengths 696·56 and 705·64. On passing the current the traces of nitrogen bands soon disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs owing to what I have called "electrical evaporation,"[*] and I think the residual nitrogen is absorbed by the finely-divided metal. Similar absorptions are frequently noticed by those who work much with vacuum tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the circuit, the colour of the luminous discharge changes from red to a rich steel blue, and the spectrum shows an almost entirely different set of lines. It is not easy to obtain the blue colour and spectrum entirely free from the red. The red is easily got by using a large coil[†] actuated with a current of 3 ampères and 6 volts. There is then no tendency for it to turn blue.

The blue colour may be obtained with the large coil by actuating it with a current of 3·84 ampères and 11 volts, intercalating a jar of 50 square inches surface. The make-and-break must be screwed up so as to vibrate as rapidly as possible. The red glow is produced by the positive spark, and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen.[‡] In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow 80 lines, making 199 lines in all; of these, 26 appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor Ramsay I was allowed to take some vacuum tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminium terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, contaminated by a trace of nitrogen

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[*] *Roy. Soc. Proc.*, vol. l, p. 88, June, 1891.

[†] The coil used has about sixty miles of secondary wire, and when fully charged gives a torrent of sparks 24 inches long. The smaller coil gives six-inch sparks when worked with six half-pint Grove cells.

[‡] Photographs of the different spectra of argon, and other gaseous spectra for comparison, were projected on the screen.

bands. The next day the tube with platinum terminals was unchanged, but that having aluminium terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour's sparking and a few days' rest the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is sparked in a tube made of pure fused quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum tube was filled with pure argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8·84 ampères and 11 volts; no jar was interposed. At a pressure of 3 m.m. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until at a pressure of about half a m.m. flashes of blue light made their appearance. At a quarter of a m.m. the colour of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of 52 m.m. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction current from the large coil for eight hours before any change was noticed. The last time when photographing its spectrum difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The colour immediately changed from the reddish yellow of nitrogen to the blue of argon, and on applying the spectroscope the lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty and by employing a very small jar I was able to take one photograph of its spectrum and compare it with the spectrum of argon from Professor Ramsay, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through, except by employing a dangerously large current. Whenever a flash passed it was of a deep blue colour. Assuming that the atmosphere contains 1 per cent of argon, the 3 m.m. of nitrogen originally in the tube would contain 0·03 m.m. of argon. After the nitrogen had been absorbed by the spattered platinum, this pressure of argon would be near the point of non-conduction.

In all cases when argon has been obtained in this manner the spectrum has been that of the blue-glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark: partly also on the degree of exhaustion. It is not improbable, and I understand that independent observations have already led the discoverers to the same conclusion—that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum tubes containing rarefied nitrogen which show either the fluted band or the sharp line spectrum by simply turning the screw of the make-and-break: exactly as the two spectra of argon can be changed from one to the other.

I have prepared tubes containing other gases as well as nitrogen at different pressures, and have examined their spectra both by eye observations and by photography. The sharp line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed will show that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at wave-length 531·7, the aurora line at 557·1, and the helium line at 587·5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapour yield spectra at all like those of argon, and the apparent coincidences in some of the lines, which, on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. As far, therefore, as spectrum work can decide, the verdict must be that Lord Rayleigh and Professor Ramsay have added one, if not two, members to the family of elementary bodies.

"*The Liquefaction and Solidification of Argon.*" By Dr. K. Olszewski, Professor of Chemistry in the University of Cracow.

Having been furnished, by Professor Ramsay's kindness, with a sample of the new gas, argon, I have carried out experiments on its behaviour at a low temperature and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

The argon sent by Professor Ramsay amounted to 300 c.c. It was contained in a hermetically sealed glass bulb, so constructed that it could easily be transferred, with no appreciable loss, into the carefully dried and vacuous apparatus in which the proposed experiments were to be performed. The argon with which I was supplied had, according to Professor Ramsay's statement, been dried with phosphoric anhydride; its density was 19·9 ($H = 1$); and he thought that at the outside it might contain 1 to 2 per cent of nitrogen, although it showed no nitrogen spectrum when examined in a Plücker's tube.

Four series of experiments in all were carried out, two with the object of determining the critical temperature and pressure of argon, as well as measuring its vapour pressure at several other low temperatures, while two other series served to determine its boiling- and freezing-points under atmospheric pressure, as well as its density at its boiling-point.

A detailed description of these experiments will be given in another place; I shall here give only a short description of the manner in which they were made.

For the first two experiments I made use of a Cailletet's apparatus. Its metallic manometer had been previously compared with the readings of a mercury manometer. As cooling agent I used liquid ethylene, boiling under diminished pressure. The glass tube of Cailletet's apparatus was so arranged that the portion immersed in the liquid ethylene had comparatively thin walls (not exceeding 1 m.m.), so as to equalise the external and internal temperature as quickly as possible.

In both the other experiments the argon was contained in a burette, closed at both ends with glass stop-cocks. By connecting the lower end of the burette with a mercury reservoir, the argon was transferred into a narrow glass tube fused at its lower end to the upper end of the burette, and in which the argon was liquefied, and its volume in the liquid state measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

Determination of the Critical Constants of Argon.

As soon as the temperature of liquid ethylene had been lowered to −128·6°, the argon easily condensed to a colourless liquid under a pressure of 38 atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished at the following temperatures and corresponding pressures:—

Expt.	Temperature.	Pressure.
1.	−121·2°	50·6 atmos.
2.	−121·6	50·6 ,,
3.	−120·5	50·6 ,,
4.	−121·3	50·6 ,,
5.	−121·4	50·6 ,,
6.	−119·8	50·6 ,,
7.	−121·3	50·6 ,,

In all seven determinations the critical pressure was found to be 50·6 atmospheres; but determinations of the critical temperature show slight differences. In experiments Nos. 3 and 6 less liquid argon was present in the tube than in the other five; in these the volume of liquid exceeded the volume of gas.

In determining the vapour pressures of argon, a tabular record of which is given below, I noticed slight differences of pressure according as I produced more or less of the liquid at the same temperature. This proved that the sample of argon contained an inconsiderable admixture of another gas, more difficult to liquefy; it is doubtless the trace of nitrogen previously referred to. The mean of the seven estimations of the critical temperature is −121°, and this may be taken as the critical temperature of argon.

At lower temperatures the following vapour pressures were recorded:—

Expt.	Temperature.	Pressure.
8.	−128·6°	38·0 atmos.
9.	−129·6	35·8 ,,
10.	−129·4	35·8 ,,
11.	−129·3	35·8 ,,
12.	−129·6	35·8 ,,
13.	−134·4	29·8 ,,
14.	−135·1	29·0 ,,
15.	−136·2	27·3 ,,
16.	−138·3	25·3 ,,
17.	−139·1	23·7 ,,

In Experiments Nos. 9, 10, and 17, the quantity of liquefied argon was very small, for it filled the tube only to a height of 3 to 5 m.m., and in the other experiments the column of liquid argon was 20 m.m. high or more.

Determination of the Boiling and Freezing Points.

Two hundred c.c. of liquid oxygen, prepared in my large apparatus,* was poured into a glass vessel with quadruple walls, so as to isolate the liquid from external heat. After the liquid oxygen had been thus poured under atmospheric pressure, a great part of it evaporated, but there still remained about 70 c.c., boiling under atmospheric pressure. A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in the boiling oxygen. At this temperature (−182·7°*) on admitting argon, no appearance of liquefaction could be noticed, even when compressed by adding a quarter of an atmosphere pressure to that of the atmosphere. This shows that its boiling-point lies below that of oxygen. But on diminishing the temperature of the liquid oxygen below −187° the liquefaction of argon became manifest. When liquefaction had taken place I carefully equalised the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling-point of argon under atmospheric pressure. Four experiments gave the numbers −186·7°, −186·8°, −187·0°, and −187·3°. The mean is −186·9°. which I consider to be the boiling-point under atmospheric pressure (740·5 m.m.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure, was 95·5 c.c.; the quantity of liquid corresponding to that volume of gas was approximately 0·114 c.c. Hence the density of argon at its boiling point may be taken as approximately 1·5. Two other determinations of the density of liquid argon, for which I employed still smaller quantities of the gas, yielded rather smaller numbers. Owing to the small amount of argon used for these experiments, the numbers given cannot lay claim to great exactness; yet they prove that the density of liquid argon at its boiling point (−187°) is much higher than that of oxygen, which I have found, under similar conditions, to be 1·124.

By lowering the temperature of the oxygen to −191° by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting point gave the numbers: −189·0°, −190·6°, −189·6, and −189·4°. The mean of these numbers is −189·6°; and this may be accepted as the melting point of argon.

In the table below I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

As can be seen from the appended table, argon belongs to the so-called "permanent" gases, and, as regards difficulty in liquefying it, it occupies the fourth place, viz., between carbon monoxide and oxygen. Its behaviour on liquefaction places it nearest to oxygen, but it differs entirely from oxygen in being solidifiable; as is well known, oxygen has not yet been made to assume a solid state.

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that at which oxygen liquefies. Its unexpectedly low critical temperature and boiling point seem to have some relation to its unexpectedly simple molecular constitution.

Name.	Critical temperature.	Critical pressure.	Bolling point.	Freezing point.	Freezing pressure.	Density of gas.	Density of liquid at boiling point.	Colour of liquid.
	Below	Atmos.			M.m.			
Hydrogen (H_2)	−220·0°	20·0	?	?	?	1·0	?	Colourless.
Nitrogen (N_2)	−146·0	35·0	−194·4°	−214·0°	60	14·0	0·885	,,
Carbonic oxide (CO) ..	−139·5	35·5	−190·0	−207·0	100	14·0	?	,,
Argon (A_1)	−121·0	50·6	−187·0	−189·6	?	19·9	Abt. 1·5	,,
Oxygen (O_2)..	−118·8	50·8	−182·7	?	?	16·0	1·124	Bluish.
Nitric oxide (NO) ..	− 93·5	71·2	−153·6	−167·0	138	15·0	?	Colourless.
Methane (CH_4)	− 81·8	54·9	−164·0	−185·8	80	8·0	0·415	,,

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* *Bulletin International de l'Academie de Cracovie*, June, 1890; also Wiedemann's *Beiblätter*, xv., p. 29.

* I have re-determined the boiling-point of oxygen, using large quantities of oxygen, and a hydrogen thermometer of much larger dimensions than previously. The registered temperature is 1·3° lower than that which I previously recorded.

Professor **RAMSAY** exhibited two sealed glass tubes which, he said, contained argon, and handed them round. He said that he had been asked by some of his friends to show them the gas. It was, however, quite invisible.

The **PRESIDENT**—It will be a satisfaction, I am sure, to anyone present to have one of these tubes in his hand, and to have really handled a glass vessel containing argon.

Dr. **ARMSTRONG** (President of the Chemical Society) —I am sure, sir, I can say at once that all present to-day who are able to judge of a communication of this kind, and all others outside, will gladly join in the chorus which Mr. Crookes has proposed should be sung. But I should like, speaking more on behalf of the chemists—and I am sure that Professor Ramsay will come over to me for the time and dissociate himself from his colleague —to say that we feel especially indebted on this occasion to Lord Rayleigh, not only on account of the extraordinarily important information which he has placed at our disposal, but more particularly on account of the example which he has set us. You, sir, very fully alluded in your address this year to the patient manner in which Lord Rayleigh had tracked this new element to its home. I feel sure that the words which fell from you will meet with the warmest approbation everywhere where such work can be understood. (Applause). The case contained in the paper is undoubtedly a very strong one. Of course, in the hurry of a meeting like this, it has not been so logically brought forward by the reader of the abstract as it might have been, in order to do it full justice; but yet I think it will be quite clear to all who have listened to him that there is a very strong body of evidence which makes it certain that there is in the atmosphere a constituent which has long been overlooked, and a constituent having most extraordinary properties. The paper is not one which, so far as the experimental facts are concerned, can be criticised here. No doubt it will meet with very considerable criticism throughout the world. People will not be satisfied to take all these statements for granted without checking them, and I have not the least doubt that very soon we shall have abundant confirmations of the correctness of the discovery. But, apart from the facts which are brought forward in this paper, there is a portion which is purely—one almost might say, if I may be allowed the expression on such an occasion—of a wildly speculative character; that is the portion dealing with the probable nature of this new element. Professor Ramsay, in his remarks, in a measure let the cat out of the bag in a way which is not apparent when you read the paper, because it is quite clear that, after all, the authors of this communication are not so entirely satisfied with the evidence to be adduced from the application of the Clausius method for the determination of the atomicity of the gas. I think that they have not sufficiently taken into account, in dealing with this evidence, the extraordinary property that this gas possesses. Nitrogen we know is a very inert form of matter, but we know that the character of nitrogen derived from its study in the atmosphere is of an altogether wrong character. We know perfectly well that, taken as an element and treated as an atom, nitrogen is probably one of the most active forms of matter known to us, and that the great difficulty we have in bringing about its association with fresh elements, when we deal with that gas, arises from its extreme activity — its extreme fondness for its own self. Now, if we can judge anything at all from the properties which we know belong to this new element, it is, I imagine, that it is like nitrogen, but "much more so." It is quite conceivable that the condition which Professor Ramsay pointed out as being the only alternative to the one which is apparently accepted by the authors of the communication is a conceivable condition. It is quite likely that the two atoms exist so firmly locked in each other's embrace that there is no possibility for them to take notice of anything outside, and that they are perfectly content to roll on together without taking up any of the energy that is put into the molecule. There is a great deal to justify a view of this kind. Of course it cannot be discussed independently of what has been said with regard to the new gas being a mixture; but it is quite clear that, as the discussion has gone on, the statements made in the paper are not so thoroughly accepted as one would think that they were. Mr. Crookes evidently wavers very much on this point with regard to there being two elements present, and I gather as much from Professor Ramsay's account. If we think that we are dealing with two gases here on the evidence of the spectroscope, there is no reason why we should not come to the same conclusion with regard to nitrogen and hydrogen. Oxygen, I believe, has three or four spectra, so that the spectroscopic evidence, after all, although it may be in a measure remarkable, does not appear to justify such a conclusion. The great difficulty that we have, I take it, in accepting the conclusion that we are dealing with an element having a molecular weight of 40 and an atomic weight of 40 arises from the difficulty of placing an element of that kind, which practically seems to me to have driven the authors to the conclusion that, possibly, they are dealing with a mixture. The difficulty would be got over, of course, if we were dealing with a complex body, and I think that was rather hinted at by Professor Ramsay when he referred to one of Olszewski's numbers. This low value, high as it is in comparison with that of nitrogen obtained from the density of the liquid, is a reason which would induce us to place it higher up in the scale of elements, and give it a lower weight. Of course these are all matters which must be discussed later on more fully: they are matters which can only be discussed very gradually, as we learn more about this substance. As regards its inactivity, very possibly that may be exaggerated. It is very difficult in a case like this to find out what are the best conditions to make use of. We know perfectly well that, if we were not in possession of the electric spark, we could scarcely have discovered that nitrogen might be combined with hydrogen to form ammonia direct. We know that we can only bring about the combination of the two if we are in a position at once to remove the product; and that sort of thing may well obtain in a case like this. We know very well that there are comparatively few substances which can be directly associated with nitrogen. It is quite likely that here we are dealing with an element which has still fewer affinities, but it does not follow by any means yet—nor do the authors assert such to be the case—that we are dealing with an element which is entirely inactive even in the form in which it is presented to us. This is not the occasion to discuss the matter fully, but these are points which certainly deserve consideration, and they are some of the first points which make this element of such importance and interest to us as chemists. In conclusion, I can only heartily congratulate the authors on having given us this communication.

Prof. **RÜCKER** (President of the Physical Society) — I think it is very important on this occasion that we should remember that this is a discussion meeting of the Royal Society, a meeting held in this way for the first time, and a meeting at which reporters are present in order that the net result of the discussion shall go out at once to the world. It is therefore, I think, extremely important that we should distinguish as clearly as possible between the various points of doubt which still may remain with regard to the new element which has been described to-day, and the one certain fact which comes out indisputably from the facts which have been laid before us, namely, that in spite of the doubt which may have existed on the matter for the last few weeks or months, we have it now beyond all question—and I quote the words of the President of the Chemical Society in saying so—that it is certain that we have here a new constituent of the atmosphere. What the importance of this is has already been mentioned, and I want once more to emphasize the fact that this central feature stands out quite clear, apart from whether we have one or two, and apart altogether from whether the various physical quantities which have been laid before us to-day have been measured with the accuracy which may be obtained in the future. But there is one particular point to which I should like to refer. It seems to me that one of the most interesting results arrived at from the physical point of view is the fact that the gas is monatomic. Some of us have had the opportunity of seeing the paper before it was read to-day, and we are therefore, perhaps, aware of one or two facts which, I think, were not actually mentioned by Professor Ramsay. One of these facts is that the experiments required to determine the ratio of the two specific heats were made twice over, or many times over, for all I know, but made in two different ways. They were made in a narrow tube, and they were made in a wide tube; and further check experiments were carried on in which other gases were compared with the new element. There can be no possibility of doubt as to a result of this sort when the experiments are carried out by two such men as Lord Rayleigh and Professor Ramsay. The matter is one which admits of no mistake when conducted in this way, and it must be accepted as certain that the element has that particular ratio of specific heats. Well, then the question arises, What follows from this? I think that it has not, perhaps, been quite sufficiently pointed out that, in order that this ratio may be obtained if we are to use the ordinary mechanical theory of gases, it is necessary that the atom with which we are dealing should be regarded as spherical. Of course, I am well aware that our pictures of spherical atoms and the like are, no doubt, only approximations to the truth; but if we are to conceive this atom as consisting of two which are closely united the one with the other, we must nevertheless suppose, from that point of view, that they are so united as to form a sphere. That is only one way of putting it, but, nevertheless, it does create a difficulty which, I think, has not been altogether referred to before. I can only, in conclusion, say that, whatever the effect may be upon the great chemical generalisation of Mendeleeff, that is, after all, an empirical law which is based at present upon no dynamical foundation. If it holds its own in this case, it will, of course, strengthen our belief in it, but, on the other hand, I do not think that it stands on the footing of those great mechanical generalisations which could not be upset without upsetting the whole of our fundamental notions of science.

The President—Among those present I am sure those who understand most of the subject will be anxious to speak. I now ask any person present to make remarks, and especially to ask questions.

Professor Roberts Austen—I should like to say that, when this beautiful discovery was communicated to the British Association, I ventured to point out that it was not too soon to consider its relation to the great metallurgical industries in which air is largely employed. In the Bessemer process alone you take some 10 tons of iron and put it into a vessel called a converter. It is melted, and air is passed through to remove the carbon, silicon, phosphorus, and other impurities. That means that no less than 100,000 cubic feet of air pass through the metal. Therefore 1000 cubic feet of argon have gone somewhere. Now, I have taken Bessemer-blown metal which has been treated with ferro-manganese, and have pumped out forty times its volume of gas, of which one-twentieth was nitrogen. In that nitrogen I have not been able to detect any argon that could not have come from the water which was necessarily used in the manipulation. I have taken a small quantity of air, and abstracted argon from it, and obtained exactly the proportion that the authors say it contains, so I am perfectly certain that the manipulation is correct. But it remains to be seen whether the argon finds its way into the iron, as nitrogen undoubtedly does, and, if it does, whether it stays there, because there are certain peculiarities that make Bessemer metal different from other kinds of steel, and it would be most interesting if we could succeed in tracing it to some of this 1000 cubic feet of argon, which has either passed into the air or into the iron. I should just like to say that I could have wished that the authors of the paper had dialysed the air through india-rubber, and not have merely used clay pipes. As one so long associated with Graham, I can only say how delighted he would have been had he known that his method would have been used by the authors of this paper, one of whom occupies Graham's own chair at University College.

Lord Rayleigh—I have very little to add to the account which my colleague, Professor Ramsay, has given of this research. The research has been, in many respects, a very difficult one. I am not without experience of experimental difficulties, but certainly I have never encountered them in anything like so severe and aggravating a form as in this investigation. Every experiment that one attempts takes about ten days or a fortnight to carry out to any definite conclusion, and the result has been, of necessity, much less progress than we could have hoped for, and many of the questions have been left open which we could have wished to settle. One such question has just been alluded to by Professor Roberts-Austen, namely, the character of the gas transfused through indiarubber. That experiment has been upon our programme, I may almost say from the first, but hitherto time has not been found to carry it out. The difficulties of those parts of the research with which I have been more particularly connected have been very great. The preparation of the gas in sufficient quantity to experiment with at all has been no easy matter, and some of the results, such as those relating to the density of the gas, are consequently not so satisfactory and not so thoroughly elaborated as one could have wished. One point that has been mentioned relates to the argument in favour of the monatomicity of the gas. Of course, what is directly proved by the experiment, if it is good, is that the whole, or nearly the whole, of the energy put into the gas, when it is heated, is devoted to increasing the energy of its translatory motion, and that no margin remains over, as in the case of other gases, to be attributed to intermolecular or interatomic motion. At first sight it seems rather a strange thing that there should be no rotation in the molecules of the gas. How can it be? Can they be without rotation, or can the energy of their rotation be so small as to be negligible in comparison with the energy of the motion as a whole? That is a difficulty which I think has not been thoroughly met hitherto by the cultivators of the dynamical theory of gases; but apparently here we may accept it that no such energy exists, or that no such energy exists in any appreciable degree. Of course that condition is quite well met by the suggestion which has been put forward, and which has also been communicated to us by Professor Fitzgerald, of Dublin, who writes as follows:—

"The reason why the ratio of specific heats of 1·66 is supposed to prove monatomicity in a gas is because in a monatomic gas there are no internal motions of any consequence. Now, if the atoms in a molecule are so bound together that hardly any internal motions exist, it would, so far as specific heat is concerned, behave like a monatomic element. That the atoms in argon may be very closely connected seems likely from its very great chemical inertness. Hence the conclusion from the ratio of its specific heats may be, not that it is monatomic, but that its atoms are so bound together in its molecule that the molecule behaves as a whole as if it was monatomic."

That argument is no doubt perfectly sound, but the difficulty remains how you can imagine two molecules joined together, which one figures roughly in the mind, and I suppose not wholly inaccurately, as somewhat like two spheres put together and touching one another—how it would be possible for such an excentrically-shaped atom as that to move about without acquiring a considerable energy of rotation. That is difficult, and I think the only interpretation is, that the gas is monatomic. No doubt the whole subject is one about which we know exceedingly little, mercury vapour being the only other gas at present which exhibits a similar property. I am not sure that any other point has been raised, but if any questions are asked Prof. Ramsay and myself are quite ready to give further explanations, so far as it is in our power to do so.

The President — I wish to make a remark, not as from the chair, but with reference to the question which is now before us, as to the condition under which the ratio of the specific heats could be exactly $1\frac{2}{3}$rds. I do not admit that a spherical atom could fulfil that condition. A spherical atom would not be absolutely smooth. In other words, it must be a Boscovitch point. Neither can I admit that excessively rigid connection between two atoms could give it the quality of having no capacity whatever for a relative vibratory movement. It would need infinitely stiff connection to give it no capacity for relative vibratory movement; and if it had infinitely stiff relative connection the connection of the two bodies would be indissoluble, and they would remain one. In fact, I think that the only kind of atom that we can conceive as giving, in the dynamical theory of heat, rigorously the ratio of $1\frac{2}{3}$rds for the specific heat is the ideal Boscovitch mathematical point endowed with the property of inertia, and with the other property of acting upon neighbouring points with a force depending upon distance. I have now to ask for any further remarks. I do not wish to closure this most interesting discussion. I hope we shall have further discussion and further questions.

If there are no more remarks and no questions to be put, I desire now, in the name of the Royal Society, to thank the Senate of the University of London for their hospitality on this occasion, a hospitality which I am sure we have all very much enjoyed. I have great pleasure in joining with the President of the Chemical Society and the President of the Physical Society in congratulating Lord Rayleigh and Professor Ramsay on the brilliant success already obtained. (Great cheering.) I join with my brother Presidents in wishing them more and more success in the continuation of their work, and in thanking them heartily in the name of the Royal Society for the communication which they have given us this day. (Cheers).

NOTICES OF BOOKS.

Elementary Practical Chemistry, Inorganic and Organic. By J. T. Hewitt, D.Sc., Ph.D., F.C.S., and F. G. Pope. London: Whittaker and Co.

This pamphlet extends to 42 pp., and is offered at the modest price of ninepence. We fail to find in it any distinctive feature as compared with other elementary treatises of its class. In a table of the solubility of salts we find it stated that lead sulphate is insoluble in water and *acids.* Experiment will convince the student that this is not the case.

The Eighth International Congress of Hygiene and Demography. Resolutions Accepted or Received by the Closing Meeting held September 9, 1894.

This report of the final Proceedings at the International Hygienic Congress is drawn up in a variety of European languages, those of Spain, Portugal, Holland, and Scandinavia being excluded. The English used is of a rather peculiar character, but it may be understood by a comparison with the French and German.

Some of the desiderata laid down concerning the supervision of diphtheria are excellent and deserve to receive legislative sanction at an early date. We fear, however, that they will be energetically opposed where elementary education is conducted on the "payment by results" system (falsely so called). Shall we ever have in every School-board a physician armed with the necessary authority concerning sanitary questions?

Very important was the proposition made by Miss Florence Nightingale on Village Sanitation in India. Many towns and villages there are in a condition which would involve disastrous results even in the cold climate of Britain. In India the co-operation of the natives can scarcely be hoped for as long as superstition leads them to drink the water of holy wells, which are in reality strong sewage, and to use the same waters for cookery and for bathing. In Australia and South Africa the neglect of sanitary precautions is alarming.

In the Sixteenth Section Prof. Than urges that the "composition of bodies should be expressed not as at present in percentages, but according to atomic and molecular quantities as units." The author seems to have overlooked the fact that the substances which have to be analysed for sanitary purposes are, for the most part, not chemical individuals, but mechanical mixtures liable to constant fluctuations.

The questions discussed in the Nineteenth Section, and the views expressed, are too decidedly political to come under our notice.

CORRESPONDENCE.

A REVOLUTION IN VOLTAIC ELECTRICITY.

To the Editor of the Chemical News.

Sir,—Under the above title, in an article in the Chemical News (vol. lxxi., p. 2), Mr. H. N. Warren claims to have discovered a new and remarkable primary battery. It is to be regretted that the discoverer did not give some definite quantitative results obtained from the battery, or else give specific directions for making the battery, so that his results could be verified by others. If, for instance, he had given the capacity in watt-hours per pound of zinc consumed, and the rate of discharge in watts that could be steadily maintained by a battery of specific dimensions or weight, it would have been more interesting to the electrical engineer than the statement that the arc produced between carbon points was "more than the naked eye could bear," or that it heated and melted metals "in quantity."

Such methods of measuring energy are so common with discoverers of batteries destined to "revolutionise voltaic electricity" that the claims are likely to be accepted with some salt.

The claims, both as to cost and electromotive force, taken in connection with his meagre description of the battery, are, to say the least, remarkable. His admission that one of the elements is zinc and the other platinum is significant as to what the economy of the battery can be. And the statement that the "outer cell contains a specially prepared manganic salt" accounts satisfactorily for something over two of his three volts. At the same time it dashes our hopes as to anything new or revolutionary.—I am, &c.,

C. J. Reed.

The Reed Electric Company, 441, Chestnut Street,
Philadelphia, Jan. 16, 1895.

Royal Institution.—On Thursday afternoon, Feb. 14, Mr. L. Fletcher, F.R.S., Keeper of Minerals at the British Museum, will begin a Course of Three Lectures on "Meteorites."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 1, January 7, 1895.

At the opening meeting A. Cornu was elected Vice-President for the year. The inaugural discourse was delivered by the retiring President, Maurice Loewy. The new President is M. Marey.

Preparation of Sprouting Graphites in the Electric Furnace.—Henri Moissan.—The sprouting may be ascribed to an abrupt escape of gas expanded by heat. The author's experiments prove that the sprouting graphites produced in laboratories may be as numerous as those met with in nature. They will also enable us to explain the formation of the natural sprouting graphites, some of which yield, as it is known, ashes most commonly very rich in iron oxide. These graphites seem to have been produced at a high temperature, without great pressure, in the midst of masses of iron which seem to have disappeared from the action of gaseous acids. Graphite resists most chemical agents. At dull redness it is not affected by watery vapour and air. It is thus found separated from its metallic gangue, and has formed masses where it has been disseminated in the rocks. From all these experiments we may conclude that a sufficient rise of temperature converts any variety of carbon into graphite, whether sprouting or not sprouting. Certain compounds, in particular iodised substances, may determine this transformation at a lower temperature, as it has been shown by Berthelot. These are reactions comparable to those of iodine upon ordinary phosphorus, which admit of polymerisation being produced earlier without modifying the general direction of the phenomenon.

Nomination of a Correspondent for the Section of Mineralogy.—M. Matheron was elected by a large majority, *vice* Scacchi, deceased.

A Special Committee has been nominated to consider a memoir by J. H. West, on the question "Why do cats always fall on their feet?"

Utilisation of the Temperature of the Critical Point of Liquids for the Recognition of their Purity.—Raoul Pictet.—We find, from the instances given, that the critical point is much more sensitive than the boiling-point. The displacement is always in the same direction for the temperature of the critical point and the point of ebullition. The addition of liquids which are more volatile and dissolve readily lowers the temperature, as in the case of aldehyd added to pental. On the contrary, the admixture of pure chloroform, boiling at 61° with alcohol, which is less volatile, lowers the temperature of the critical point. Chlorethyl boiling at +11° has its critical point raised by the addition of a few drops of alcohol which boils at 78·8°. These experiments have been continued on ether, alcohol, and mixtures of solids in solution.

Qualitative Separation of Nickel and Cobalt.—A. Villiers.—Already inserted.

Revue Universelle des Mines et de la Metallurgie.
Vol. xxviii., No. 2.

Composition of Atmospheres which Extinguish Flame. — Prof. Frank Clowes, D.Sc. — A paper read before the Royal Society.

Electricity in Chemical Industries. — Electricity is more and more employed in chemical industry in the moist way, for the production of potassa, soda, chloride of lime, potassium chlorate, ozone, the chromates and permanganates, white lead, hydrogen and oxygen, &c. The establishment at Griesheim, near Frankfort, treats KCl in order to produce potassa and calcium chloride. The secret lies in the nature of the diaphragms which separate the kathodes from the anodes, and which allow the electrolysis to be effected without increasing the resistance, and consequently the tension. The electrodes are in general of platinum, retort-coke, lead peroxide, iron sulphide, phosphides or silicides, and polarisation is combatted by chemical and mechanical means. Kathodes of mercury allow of the electrolysis of solutions of KCl even without diaphragms. On treatment with hot water the amalgam yields caustic potash and mercury. The Associated Works at Leopold's Hall use parchment-paper as a diaphragm. To the liquid at the anodes they add 2 per cent of calcium or magnesium chloride, which, on contact with the alkaline liquid of the kathodes, forms a preservative deposit of basic chlorides upon the parchment-paper.—*Berg und Hutten Zeitung* (No. 48, 1894).

MISCELLANEOUS.

City and Guilds of London Institute.—The Executive Committee of the City and Guilds of London Institute have awarded the first Salters' Company's Research Fellowship for the encouragement of Higher Research in Chemistry in its relation to Manufactures to Martin O. Foster, Ph.D., F.C.S. Dr. M. O. Foster was a student at the City and Guilds Technical College, Finsbury, during three sessions (1888—1891), and subsequently graduated Doctor of Philosophy (*magna cum laude*) at the University of Würzburg. For several months he has been engaged in investigating some new derivatives of camphor in the Research Laboratory of the City and Guilds Central Technical College, and by the aid of the Salters' Company's Research Fellowship he proposes to pursue this line of work.

Institute of Chemistry of Great Britain and Ireland.—Names of the candidates who passed the examination held in January, 1895:—A. E. Bell, Owens College, Manchester, and Royal College of Science, South Kensington; C. S. Ellis, Owens College, Manchester, and University College, Aberystwith; M. O. Forster (Ph.D., Leipzig), Finsbury Technical College; J. Lones, Mason College, Birmingham, and Registered Student under A. E. Tucker, F.I.C.; G. H. Russell, Yorkshire College, Leeds; W, H. Sodeau, King's College, London; W. L. Sutton, University College, London; W. G. Young, University College, London, and Registered Student under W. C. Young, F.I.C. Examiners:—Professor Wyndham R. Dunstan, M.A., F.R.S., F.I.C., and Thomas Fairley, F.I.C.

Study on Oil of Cananga.—A. Reychler.—The density of this essential oil at 21° is 0·9058, and the index of refraction $n = 1{\cdot}49655$. Its levo-rotation $[\alpha]_D = -28{\cdot}5°$. Its compostition is C, 85·68; H, 11·81; O, 2·51. Oil of cananga has a great resemblance to ylang-ylang, but it is clearly distinguished from the latter by containing a much larger proportion of sesqui-terpene. [It is to be regretted that French scientific journals often insert a memoir without indicating clearly at the beginning or the end that it has already appeared in some other journal or has been read before some learned society].—*Bull. Soc. Chimique.*

Novelist's Chemistry.—We have occasionally had occasion to twit contemporary novelists with striking and sometimes amusing ignorance of anatomy and physiology. Their chemistry is not always above suspicion; witness the late Mr. Florence, who makes prussic acid play a lethal *rôle* in one of his stories, the acid in question having been stolen from one of the "carboys standing at the door of the drug store." In one of the Christmas stories the detection of the murderer was contributed to by a witness having accidentally "caught a whiff of the strychnine" on applying his nose to the bottle. Sharp nose that!—*Medical Press.*

The Solubility of Phenyhydrazin in Watery Solutions of the Alkaline Salts of the Sulphinic, Sulphonic, Fatty, and Biliary Acids.—Robert Otto.—The author finds on examining the phenylhydrazin salt of β-naphthylsulphinic acid, prepared from its constituents in a solution of methyl-alcohol, that the product is soluble in potassa lye without separation of phenylhydrazin. It appeared that the phenylhydrazin salt is not capable of decomposition by aqueous potassa lye, is not decomposed with precipitation of phenylhydrazin, because the base, soluble in water only in a slight degree, and almost insoluble in concentrated potassa lye, is readily soluble in an aqueous solution of alkaline naphthylsulphinate. If phenylhydrazin is added to such a solution it dissolves completely on shaking, forming a liquid which is miscible with phenylhydrazin in any proportion. Phenylhydrazin is insoluble in a solution of sodium ethylsulphinate. The same behaviour was observed with phenylhydrazin in contact with aqueous solutions of the alkaline salts of the aromatic sulphonic acids, the higher fatty acids (soaps), and the biliary acids. The author mentions an analogy between phenylhydrazin and the phenols. Like the former base these compounds become soluble in water by the mediation of soap, sodium salicylate and kresotinate, sodium kresol, &c. The disinfectants sold under the names sapocarbol, lysol, salveol, &c., belong to this class.—*Berichte*, xxvii., p. 2131.

The Oyster Panic.—According to *Science* the origin of the present panic is as follows:—Professor H. W. Coun described in the *Medical Record* of December 15th last twenty-six cases of typhoid which had occurred in October and November at the Wesleyan University. The first cases among the students appeared on October 20th, and seemed to be connected with the fraternity suppers held on October 12th. The water supply was tested, and the plumbing was examined with negative results. Nothing suspicious was traced in the food, save in case of raw oysters, obtained, as we learn by all the three fraternities, from one and the same dealer. These oysters had all been obtained from the deep water of Long Island Sound, and had been laid in the mouth of a fresh water creek to fatten. This fattening is a process of questionable honesty, since it consists merely in causing the mollusk to absorb fresh water by osmosis, thus increasing its bulk without adding to its proportion of nutritive matter. It was found that within 300 feet of the place where the oysters had been laid to fatten was the outfall of a private sewer, leading from a house where there were at the time two cases of typhoid fever. It is possible that other similar cases may have arisen elsewhere, but there is no evidence that oysters from clean water can contain the bacilli of typhoid. One inference may be drawn with certainty, that is that fishes, mollusks, and crustaceans may be highly dangerous if obtained at or near the outfall of polluted rivers, of sewers, or in places where sewage sludge is thrown into the sea. In other words, we see the impolicy of all schemes for the treatment of sewage which turn on its discharge, or the discharge of its deposits, into the sea.

MEETINGS FOR THE WEEK.

Monday, 4th.—Society of Chemical Industry, 8. "Some Matters of Interest in the Manufacture of Coal-gas," by Lewis T. Wright, C.E , F.C.S.
— Medical, 8.30.
Tuesday, 5th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "Drawing for Process Reproduction," by Gleeson White.
Wednesday, 6th.—Society of Arts, 8. "The Labour Question in the Colonies and Foreign Countries," by Geoffrey Drage.
— Geological, 8.
Thursday, 7th.—Royal, 4 30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "George Eliot, the Humourist as Poet," by W. S Lilly, M.A.
— Chemical, 8. "The Electromotive Force of an Iodine Cell," by A, P. Laurie, M.A. "The Action of Heat on Ethylic β-Amidocrotonate," by Dr. Collie. "The Acidimetry of Hydrofluoric Acid," by Prof. Haga.
Friday, 8th.—Royal Institution, 9. "The Anti-toxin Serum Treatment of Diphtheria," by G. Sims Woodhead, M.D.
— Astronomical, 3. (Anniversary).
— Physical, 5. (Annual General Meeting). "An Exhibition of Simple Apparatus," by W. B. Croft, M.A. "On the Tin Chromic Chloride Cell," by S. Skinner.
Saturday, 9th.—Royal Institution, 3. "Hansel und Gretel" (with musical illustrations) an opera by E. Humperdinck, by Sir Alexander Campbell Mackenzie, Mus. Doc.

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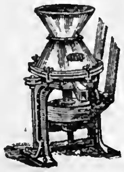

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THE CHEMICAL NEWS.

Vol. LXXI., No. 1837.

ARGON—A SUGGESTION.

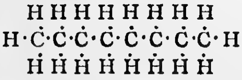
By G. JOHNSTONE STONEY, M.A., D.Sc., F.R.S.

In the examination of argon we are still at the stage of being engaged in the search for what it really is; so that it is not useless at this stage to set down all the *possible* alternatives.

And first, with respect to the ratio of the specific heats and what it implies, viz., that the energy of the "internal" motions—of motions within the individual molecules—is small. There is, as regards this, another alternative besides those presented at the meeting of the Royal Society, which is that the mass of the molecule may consist of a large mass comparatively quiescent and a small mass in active motion. In this case, as well as in those stated at the meeting, the energy involved would be small; and we should, moreover, have a state of things very much more consonant with the fact that argon emits two complex and bright spectra.

Such "internal" activity involving little energy is not unknown. It is, in fact, what occurs in the familiar phenomenon of phosphorescence, where a body has had such motions set up in some part of each molecule as are capable of emitting light for a long time, but which are so isolated from the rest of the molecule that they do not share their energy with it so as to raise the general temperature.

It may be objected that if the molecule consist of one predominant mass associated with one or more small masses, the predominant mass will absorb energy by rotating; but this is based on the supposition that it is a rigid body. Now we must remember that, though this conception of rigid bodies is so much the most convenient to the mathematician that it is universally adopted in the dynamical investigation, nevertheless such bodies are *impossible* from the physicists' standpoint, and do not exist in nature. Who that considers the connections can doubt that a molecule of the normal paraffin C_8H_{18}, which may be represented by—



$$\begin{array}{c} \mathrm{H\ H\ H\ H\ H\ H\ H\ H} \\ \mathrm{H\cdot C\cdot C\cdot C\cdot C\cdot C\cdot C\cdot C\cdot C\cdot H} \\ \mathrm{H\ H\ H\ H\ H\ H\ H\ H} \end{array}$$

is more like a long flexible thread than a rigid sphere? Now, it is easy to conceive that at the close of an involved struggle between two such molecules protracted over a time which is long when compared with other molecular activities, the conditions may be such when they part that they will sail off from one another without much rotation having been set up. Where we are misled is by the false analogy of rigid bodies, and especially by thinking of the prolonged encounter that takes place in nature with all its complex incidents, as a mere collision!

To return to our illustration. It is quite conceivable that during the journeys of such a molecule as that of the vapour of the above paraffin between its encounters, the two end atoms, or the parts of them which carry their electrons,[*] may be swinging about violently, while the rest of the system travels along without much internal agitation.

This particular illustration has been selected because it seems *possible* that by the discovery of argon we have been brought within grasping-distance of a much greater discovery; in fact, that it may in reality prove to be a compound of one of the six missing elements which lie between hydrogen and lithium—perhaps a compound somewhat like the above paraffin.

Assuming George Darwin's account of the origin of the moon, we must presume that as the moon and earth cooled down they evolved similar atmospheres, but that the potential of gravitation on the moon is too small to have enabled it to prevent the occasional escape of molecules of water, nitrogen, oxygen, and carbon dioxide; so that it has now been left without its atmosphere. In a discourse delivered before the Royal Dublin Society on December 19, 1870, the present writer called attention to this explanation of the non-existence of atmosphere on the moon, and pointed out the fact that these gases having been able to escape from the moon, involves as a necessary consequence that a body with the earth's potential of gravitation and velocity of rotation must be unable to prevent the escape of free hydrogen from its atmosphere. Hence we should have now no hydrogen on the earth were it not for the circumstance that hydrogen entered extensively into combination with other elements, and thus forms part of molecules too massive to be able to escape from the earth. The earth, in fact, is only able to hold its large stock of hydrogen as constituents of such compounds as water, ammonia, hydrochloric acid, of organic substances generally, and of some minerals. But except in a state of combination, the earth is not competent to retain hydrogen.[*] The six other elements between hydrogen and lithium seem not to have been able to enter into, or to remain in, combination under the conditions that prevailed at some stage of the earth's past history, and so then escaped—unless, possibly, a compound of some of them may yet be found.

Let us, for convenience, name them as in the accompanying Mendeleeff table.

Argon, then, may turn out to be a compound of one of these; and of them the most probable is perhaps infra-carbon. Silicon shows a slight aptitude for combining with hydrogen, and the hydride of silicon is a very active body. Carbon forms with avidity compounds with hydrogen that are so inert that one great series of them has been called "paraffins," from *parum affinis*. If this property is as much more intense in infra-carbon than in carbon, as it is more intense in carbon than in silicon, it may well result in producing a compound as impassive as argon.

Assuming that the atomic weight of infra-carbon is about 2½ or 3, then if it forms compounds similar to those of carbon, argon may be analogous to one of the paraffins C_7H_{16}, C_8H_{18}, C_9H_{20}, or to some other hydrocarbon of the fatty series, or to hydrocarbons of the benzene series, or to such compounds as naphthalene, $C_{10}H_8$; diphenyl, $C_{12}H_{10}$; turpentine, $C_{10}H_{16}$. It may even, though with less probability, be analogous to a monatomic alcohol, such as $C_4H_9\cdot OH$ or $C_5H_{11}\cdot OH$, or to some other compounds, and its inertness may be such that even substitution derivatives may be very difficult to produce.

A mere speculation such as this is only allowable under circumstances like the present—while we are feeling

Hydrogen	Infra-beryllium	Infra-boron	Infra-carbon	Infra-nitrogen	Infra-oxygen	Infra-fluorine	
Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine	
Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine	
&c.	&c.	&c.	&c.	&c.	&c.	&c.	&c.

---

[*] Electron, the fixed charge of electricity, the same in all cases, which is associated with each chemical "bond."

[*] The same method applied to Mars leads to the conclusion that it is improbable that the vapour of water can be retained by that planet, in which case we must look to some substance of greater density, such as carbon dioxide, as the material which produces the snow caps and the long streaky fogs (probably following valleys) which are from time to time seen upon Mars.

about for what argon really is. In one respect argon behaves very differently from the organic compounds of carbon, in that it is not decomposed by heat. This seems a natural consequence of the fact which has been brought to light by the ratio of its specific heats, viz., that but a small part of its heat energy takes the form of events going on within its molecules. Besides, infra-carbon is quite as likely to approximate to silicon in some of its properties as to carbon. But, above all, the hypothesis that argon is a compound has this great recommendation, that it does not involve any interruption of Mendeleeff's law, which, though only empirical, is probably true. The writer therefore hopes that this alternative possibility will be investigated along with the other, and perhaps less probable, ones that were produced at the meeting of the Royal Society.

THE NOMENCLATURE OF THE PENTOSES AND PENTOSANS.

By C. F. CROSS.

Dr. Stone's rejoinder (Chemical News, lxxi., p. 40) to my suggestion of a more neutral designation, for certain purposes, of the furfural-yielding carbohydrates, although based on a more or less obvious misapprehension of the issue which I intended to raise, leaves me no option but to elaborate the point in reply. Since my critic remarks, "it is hardly possible" that I "should be unacquainted with the terms 'pentoses' and 'pentosans' in common use to designate these bodies," there appears to be some residual apprehension of my aiming, in ignorance, a quixotic thrust at the systematic and "official" terminology of the carbohydrates. Such an intent I need not disclaim. The next paragraph of the criticism contains the fundamental mis-statement upon which the whole issue turns, and it is a wider one than appears to have been recognised. "The furfural reaction, as applied to carbohydrates, is given only by the pentatomic sugars or by certain amorphous substances which upon hydrolysis yield one or other of these sugars." On this point the author must be referred to categorical evidence to the contrary contained in recent publications (Cross and Bevan, *Ber. Chem. Gesell.*, xxvi., 2520—2533; xxvii., 1061—1065). There are, in fact, a large number of celluloses of "carbohydrate" formula, or approximately so, which give yields of furfural of from 2 to 15 per cent, which at the same time do not give the characteristic reaction (with phloroglucinol) of the pentoses and pentosans, and are further differentiated from the latter by comparative resistance to hydrolysis.

To take the controverted point for a moment out of a region which appears to involve too much of the personal element, the following parallel case may be given:—The oxidation (HNO_3) of galactose groups to mucic acid was regarded until recently as a positive and exclusive diagnosis of their presence in carbohydrates of unknown composition. It has now been shown that the methyl-hexoses are similarly oxidised to this acid. Supposing the hexoses were always referred to under a systematic terminology, under which the galactoses might be distinguished as γ-hexoses. The application of the logic of Dr. Stone's contention would lead to the extension of this term to the methyl-hexoses. Thus, if furfural-yielding carbohydrates = pentoses; mucic acid yielding carbohydrates = γ-hexoses; then pentoses = C_5-aldoses with certain hexose derivatives, &c., γ-hexoses = galactoses, methyl-hexoses, &c., which propositions are absurd. On the other hand, a neutral term such as mucose or furfurose, instead of conflicting with the systematic description, merely groups together bodies of varying composition under a common characteristic of decomposition, having sufficient significance to make it a subject of continual reference.

Having just completed a monograph on cellulose (Cross and Bevan, "Cellulose," Longmans, 1895), it has been found necessary to make free use of the terms "furfural-yielding carbohydrates," "furfural-yielding complex," &c., in describing constituents of the permanent tissues of plants, having this property in common with the pentosans, but differing in other equally characteristic reactions, and on general physiological grounds with equal probability hexose derivatives.

A year or two ago we (Cross and Bevan) expressly maintained this view of the origin of these furfural-yielding constituents of plants. Stone and de Chalmot, in approaching this subject from the point of view of the pentoses and pentosans, and using these terms as interchangeable with the above phrase description, were undoubtedly misled into the view that the pentoses were direct products of assimilation. De Chalmot has now established as the issue of an important series of investigations, and in opposition to his earlier conclusions, that these furfural-yielding constituents are products of metabolism, and derived through oxidation processes from the hexoses.

Approaching this physiological question from the point of view of systematic chemistry, there appeared, *à priori*, no cogent reason why the plant should not build up C_5 or C_7 aldoses.

Coming to the same subject under consideration of the general prevalence of the hexoses — their liability to graduated oxidation—and such products tending also to the $R.C_4O$ (furfural) condensation, we gave preference to the opposite hypothesis. We also have held the opinion that those specialists who have done such excellent work in the pentose group would not have taken up a position in regard to the assimilation problem from which they have withdrawn, but for the undue influence of terms and the assigning of final significance to a reaction of decomposition.

My suggestion still is that some neutral term should be used to designate "furfural-yielding carbohydrates" (or their immediate derivatives) not yet ascertained to be pentosans, and from their properties generally probably containing furfural-yielding groups other than those of pentose configuration.

ON THE PROTOMORPHIC STATE. ZINC AND MANGANESE SULPHIDES.

By A. VILLIERS.

We have recently pointed out certain reactions of nickel and cobalt sulphides, and have indicated some new properties of these substances which seem to us to show that at the moment of their formation they must exist in a different state from that in which we know them when once formed. This condition we propose to denominate as the *protomorphic state*.

The reactions produced in this state by the nickel and cobalt sulphides are merely an instance of reactions a certain number of which are already known, and which may be produced by bodies before they have acquired their ultimate properties, after having undergone one or more transformations probably corresponding to condensations with liberations of heat often manifested by phenomena of crystallisation.

These transformations are immediate and cannot be demonstrated by calorimetric methods, but only by chemical reactions effected at the moment of their formation. This is the case with nickel sulphide. They are either produced but slowly, say, in a few minutes, and may then be shown by the liberation of heat which goes on after the bodies constituting the original system have been brought in contact, or during several days, several years, occasionally during a time too long for the direct observation of the corresponding liberation of heat. In this latter case, which is that of a great number of precipitated oxides and salts, we may at any moment form an idea of the actual state of the substances, whether by the quantities of heat evolved when they are brought to a final, definite condition, or by the differences observed in their chemical properties.

The *protomorphism* of the metallic sulphides may be manifested by this latter method in a very great number of sulphides other than those of nickel and cobalt, and the precipitated sulphides may produce certain reactions interesting from a twofold point of view, since they indicate the existence of novel compounds, and are sometimes capable of analytical applications.

Zinc Sulphide.—The transformation of zinc sulphide is not immediate in the cold, like those of nickel and cobalt sulphides. It is very rapid in heat, but it goes on at common temperatures for several hours or more. This may be manifested by the action of the alkaline sulphides.

Professor Thomsen (*Berichte*, xi., 2044) has shown that sodium sulphide gives with a solution of zinc sulphate a precipitate of zinc sulphide; but if we substitute for the alkaline sulphide a hydrosulphate of sulphide, the zinc sulphide is still formed if we employ the latter only in equivalent quantity; but if we go on adding twice the quantity of hydrosulphate of sulphide, we obtain no precipitate, but a limpid or opalescent liquid which yields a precipitate of zinc sulphide or hydrosulphate if we add either soda or an acid.

The soluble compound of zinc sulphide and of alkaline hydrosulphate of sulphide, comparable to that of zinc oxide and potassium hydroxide, may be produced still more decidedly as follows:—

If into the alkaline liquid obtained by pouring a solution of zinc sulphate into soda until the former no longer re-dissolves, we pass a stream of hydrogen sulphide, we find that the first bubbles of the gas occasion the precipitation of the zinc as sulphide. If we continue the introduction of the gas this precipitate re-dissolves, and we obtain in a few moments a liquid completely limpid, if the solution is sufficiently dilute, *e.g.*, with a liquid prepared with solutions of soda and zinc sulphate at 10 per cent, and then diluted to one-tenth. The weak acids and alkalis still precipitate zinc sulphide; the same precipitation is produced on boiling. We have, therefore, a combination of zinc sulphide and sodium sulphide hydrosulphate.

It is easy to show, on slightly modifying the conditions of this experiment, that zinc sulphide recently precipitated undergoes a transformation.

If, after having introduced the first portions of sulphuretted hydrogen so as to precipitate zinc sulphide, we do not prolong the action of the gaseous current, and leave the mixture at the ordinary temperature of 15° to 20° after having carefully stoppered the vessel in which the precipitation has taken place, we find that after the lapse of some hours the zinc sulphide is no longer capable of being re dissolved by the action of a further quantity of hydrogen sulphide, however long we continue to pass the gas into the liquid.

This transformation may be immediate or slow according to the conditions which we shall shortly define.

Zinc sulphide precipitated in its soluble modification in sodium sulphide hydrosulphate is always amorphous. In its insoluble modification we have always found it crystalline.

The use of sodium sulphide hydrosulphide enables us to separate the amorphous sulphide from the crystalline sulphide, and to follow the march of the transformation when it takes place in a progressive manner.

We shall make it remarked, from the analytical point of view, that the above facts show how in the separation of metals we should use only alkaline sulphides and not hydrosulphates of sulphides, especially when working in the cold, and that we cannot substitute for the use of the alkaline sulphides that of hydrosulphuric acid by passing the gas into the alkaline liquid.

We see also that there may occur a source of error in the qualitative recognition of zinc, and that the precipitation of zinc sulphide by sulphuretted hydrogen in an alkaline liquid may escape observation. It is therefore well to effect this precipitation in a liquid supersaturated with acetic acid.

Manganese Sulphide.—The protomorphism of manganese sulphide cannot be manifested by the foregoing reaction, at least under the conditions in which we have been able to manifest the protomorphism of zinc sulphide.

We may even separate manganese from zinc by passing a current of hydrogen sulphide for some minutes into a liquid containing ammonia and ammonium chloride, avoiding excess of the two latter. If the dilution is sufficiently great, manganese sulphide will be alone precipitated in the cold, whilst the zinc sulphide may be found in the filtrate, and may be separated by an addition of acetic acid.

We must remember that manganese sulphide may occur in at least two very different aspects, either of a flesh-colour or of a green. The two modifications correspond to different states of hydration. The transformation of the former into the latter was discovered by Berzelius, and has been studied by Muck, and by P. de Clermont and H. Guiot. The former state may be compared to amorphous zinc sulphide, and the latter to crystalline zinc sulphide. The transformation of manganese sulphide seems to ensue in conditions analogous to those of zinc sulphide, but less easily—*e.g.*, at higher temperatures or in more concentrated solutions.

The negative indication here manifested is no proof that ordinary flesh-coloured manganese sulphide does not in turn result from the transformation of a sulphide existing in an earlier protomorphic state. — *Comptes Rendus*, cxx., p. 97.

NOTE ON THE

ESTIMATION OF SOLUBLE PHOSPHATE.

By VINCENT EDWARDS, F.C.S.

As the correct estimation of soluble phosphoric acid in manures is, now more than ever, a matter of importance, I venture to submit the following remarks, which may be of interest to chemists in manure works who desire rapid and accurate results.

It occurred to me that the differences sometimes found in the determination by competent chemists might be due to the length of time which was allowed for the precipitate of ammonio-magnesium phosphate to settle, and I therefore carried out the following experiment to clear up the point:—

I had in hand a sample of high superphosphate, known to contain between 19 and 20 per cent of P_2O_5, soluble in water; and having weighed out two quantities of 1 grm. each, treated them precisely alike, with successive washings of cold, and finally hot water, in the manner generally employed. To the clear filtrate of each 50 c.c. of citro-magnesic solution (Sutton) was added, followed by excess of ammonia, and the contents of each beaker being vigorously stirred, the precipitates were allowed to settle—No. 1 for one hour and a half, No. 2 for forty-eight hours. The precipitates were collected, washed with dilute ammonia, dried, and ignited as usual. The results were found to be — No. 1, 19·20 per cent; No. 2, 19·14 per cent P_2O_5.

From these results it would appear that the length of time in which the precipitate is allowed to settle is not of much importance; but it is interesting to note that the longer period gives slightly the less result.

As I had reason to know that the above figures are accurate, it would seem well to allow about two and a half hours for the precipitate to subside. This would not only permit the whole of the ammonio-magnesian phosphate to form, but give it also full time to settle, and render the subsequent operations more satisfactory. Two hours and a half is not long, and with an early start permits several accurate results to be returned in the evening.

It is well to add that excess of ammonia in the beaker during settling is most essential, the solubility of the precipitate being somewhat marked if this is not attended to. The complete washing of the collected precipitate is to my mind also very important; any neglect of this is a greater cause of error than anything else.

Lawes' Works, Barking, Essex,
January 22, 1895.

DERIVATIVES OF DIAMIDE WITH A CLOSED ATOMIC GROUPING.

By TH. CURTIUS.

(Continued from p. 47).

Treatise II.—*On Pyrazolin and some of its Derivatives.*

By F. Wirzing.

Hydrazin hydrate acts simultaneously in the cold upon akrolein, forming pyrazolin. The akrolein hydrazin first formed is at once transposed into pyrazolin. Akrolazin is not formed.

Pyrazolin is a volatile liquid of a decidedly basic character. It combines with the mineral acids to form salts permanent in the air. It has also the nature of a feeble acid, and it forms double compounds with the metallic salts. Pyrazolin shows its nature as an atomic chain combined in a ring by its ready transition into pyrazol in presence of bromine and by its great stability with concentrated mineral acids.

In its decomposition by acids there is a formation of hydrazin and β-lactic aldehyd. Its boils without decomposition at the ordinary pressure of the atmosphere. Pyrazolin is energetically attacked by oxidising agents with development of gases. Permanganate reacts at once in the cold. Gold chloride, ferric chloride in a neutral solution in the cold, and platinum chloride in heat, attack pyrazolin energetically with liberation of gases. It does not reduce Fehling's solution even on ebullition. Ammoniacal solution of silver in heat is gradually reduced by the free base to metal, but solution of gold chloride at once.

Pyrazolin does not display the so called pyrazolin reaction of Kron's (1)-phenylic pyrazolin derivatives. (Colouration in very dilute solutions by oxidising agents). Its salts gives in aqueous solutions a very characteristic reaction, by means of which they can be readily distinguished from those of pyrazol. In the most dilute solutions they colour lignin (woody fibre) a most intense dark yellow.

Pyrazolin takes a dark yellow colour with nitrous acid, but no nitroso-compound has as yet been isolated. It readily combines with benzaldehyd with the elimination of water. With diabenzene salts it combines to form pyrazolinazobenzene substances of a splendid red colour. Neither of these reactions is obtained with pyrazol, but with pyrazolon.

The author adds a comparative table of the characteristic reactions of pyrazol, pyrazolin, and pyrazolon.

(3)-methyl-(5)-dimethylpyrazolin is readily obtained by the action of hydrazin hydrate upon mesityl oxide in the cold. The same substance is formed, according to Curtius and Fœrsterling, by the transposition of bis dimethylazimethylen by means of maleic acid. It is a colourless oil of a powerful odour, and a decided basic character. It combines with acids, bases, and salts. The heated vapour of the free base explodes on access of air with a display of fire. Its form no azo-dye with azobenzene salts,—in contrast to pyrazolin. It gives precipitates with the solutions of various heavy metals.

During the action of phenylhydrazin upon akrolein there is formed, in addition to (1)-phenylpyrazolin, a second substance of the empirical formula $C_{24}H_{34}N_6O_{12}$.

Benzaldehyd and (1)-phenylpyrazolin combine only in equimolecular proportions. The product benzalphenylpyrazolin seems to exist in two modifications.

Nitrous acid acts upon (1)-phenylpyrazolin with formation of a brick-red isonitroso-compound,—

$$C_6H_5.C_3H_3N_2 : NOH.$$

Diazobenzene salts form with phenylpyrazolin a purple-red basic colouring matter, $(C_6H_5.N_2C_3H_4).N_2C_6H_5$, which yields a dark steel-blue hydrochlorate. The acetic solution of the pigment is reduced by zinc-powder.

The behaviour of phenylpyrazolin with hydrochloric acid is very peculiar. There is formed a compound of 2 mols. phenylpyrazolin with 1 mol. hydrochloric acid, from which the original base cannot be again separated. This product has totally modified properties, and it may be regarded as a bis-phenylpyrazolin. The constitution of the base is not yet known with certainty.

Bis-phenylpyrazolin gives red precipitates with diabenzene salts, with nitrous acid or bromine.

Allyliodide and hydrazin hydrate were caused to react upon each other in the expectation of thus arriving at pyrazolidin. The research had not the desired result.

Besides diammonium iodide as the main product, there was obtained a substance, $C_9H_{17}N_2.I$, which may be regarded as diallylpyrazolidin iodide, or as a triallylhydrazin iodide.

Pyrazolin is a colourless liquid of a characteristic faintly aminous odour which reminds us of cacao. It forms a mist with vapours of hydrochloric acid. At 144°, and at a pressure of 760 m.m., it boils without decomposition. It is volatilised along with the vapours of water and of ether. It mixes with water and alcohol in all proportions. Its composition is $C_3N_2H_6$.

The author next describes the compounds of pyrazolin with hydrochloric acid, $C_3H_6N_2.HCl$, with sulphuric acid, its chloroplatinate, $(C_3H_6N_2.HCl)_2.PtCl_4$, and its picrate.

The behaviour of pyrazolin with acids proves that it cannot be an akroleinhydrazin.

On treating pyrazolin in a reflux refrigerator with concentrated alkaline lyes, about 10 per cent of the nitrogen present is split off.

Pyrazolin is very sensitive to oxidising agents, as it has been mentioned above. The behaviour of bromine with pyrazolin or pyrazolin hydrochlorate is distinct, as they are totally converted into pyrazol.

The demonstration that the base formed from akrolein and hydrazin hydrate is a pyrazol hydride is given by the conversion of the base itself, or of its hydrochlorate into pyrazol by means of bromine in a solution into chloroform, as well as by the production of brompyrazol from pyrazolin hydrochlorate (in presence of Br ?) in an aqueous solution.

(To be continued).

Production of the Kathode Rays.—Jos. de Kowalski.—A full abstract of this memoir would require the three accompanying figures. The conclusions reached by the authors are, that the production of these rays is not connected with the discharge from the metallic electrodes through rarefied gases. They are produced whenever the so-called primary luminosity attains a considerable intensity, or, in other words, whenever the density of the lines of the current is sufficiently considerable. The direction of their propagation is that of the lines of the current in the portion where the rays are produced in the direction from the negative pole to the positive pole.—*Comptes Rendus*, cxx., No. 2.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 17th, 1895.

Dr. Armstrong, President, in the Chair.

Messrs. Cecil Cooke Duncan and Robert W. Buttermer were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Thomas Bennett Case, B.A., 82, James Street, Dublin; Henry Fairrie, 63, Parkfield Road, Liverpool; Herbert Edward Gardner, Lyonsdown Vicarage, New Barnet; Henry Tresawna Gerrans, M.A., 20, St. John Street, Oxford; George Goldfinch, Hendon, N.W.; Edgar Joseph, 42, Brondesbury Road, Kilburn, N.W.; Henry R. Le Sueur, B.Sc. (Lond.), Chemical Laboratory, St. Thomas's Hospital, S.E.; Robert Meldrum, 27, Lansdowne Road, S.W.; Henry Edward Niblett, B.A., Eldon Lodge, Hewlett Road, Cheltenham; Harry James Powell, 530, Lordship Lane, S.E.; Herbert Lewin Robinson, 9, Lloyd Street, W.C.; Harry Wilson, 146, High Street, Southampton.

The certificate of the following candidate, proposed by the Council under By-law 1 (3), was also read:—

Edward Herbert Hill, Colonial Bank of New Zealand, Dunedin.

The following is the text of the letter which has been received from Professor Remigius Fresenius, acknowledging the address recently presented to him by the Society:—

"Wiesbaden, den 6ten Januar, 1895.

"An den Vorstand der Chemical Society of London.

"Sie haben mir durch Übersendung des prachtvollen Diploms, welches mir in Erinnerung bringt, dass ich seit 50 Jahren die Ehre habe Mitglied Ihrer hochangesehenen und hochachtbaren Gesellschaft zu sein, eine grosse Freude bereitet. Das Diplom, am 24ten December des verflossenen Jahres abegesandt, wurde mir am 28ten December, als an meinem 76ten Geburtsfeste, überreicht. Gestatten Sie, das ich Ihnen für die mir gewordene Auszeichnung meinen herzlichsten Dank sage.

"Wenn man auf die 50 Jahre zurückschaut, welche zwischen meinem Aufenthalt im Liebig'schen Laboratorium in Giessen und der Gegenwart liegen, und die ausserordentlichen Fortschritte in's Auge fasst, welche die Chemie in allen ihren Gebieten und welche im Zusammenhange damit die chemische Industrie gemacht hat, so kann man diess nur mit Stolz und grosser Freude thun, denn Zeiten grösseren Aufschwungs hat keine andere Wissenschaft zu verzeichnen, und wenn man sich vergegenwärtigt, dass dieser Aufsschwung dem Zusammenwirken der Forscher der verschiedenen Culturvölker zu verdanken ist, so gereicht diess zu besonderer Genugthuung. Ist es doch in Wahrheit eine Freude sagen zu können, es gibt noch Gebiete, auf denen die Nationen sich nicht bekämpfen, sondern auf denen sie sich zur Förderung gemeinsamer Interessen und zur Errechnung gemeinsamer Ziele freundlich die Hände reichen.

"Es war mir vergönnt an der Lösung der Aufgaben der Chemie 5 Decennien hindurch mitwirken zu können und ch freue mich dessen von ganzem Herzen, und wenn ich auch jetzt den Fortschritten der Wissenschaft nicht mehr in allen ihren Theilen zu folgen vermag, so bin ich doch aufrichtigen Dankes voll, dass mir immer noch Lust, Liebe und auch eine gewisse Kraft geblieben ist in meinem 77ten Lebensjahre an der Förderung der analytischen Chemie mitarbeiten zu können.

"Ihr schönes Diplom schliesst mit dem freundlichen Wunsche, dass mir diese Mitarbeit noch langere Zeit vergönnt sein möge und verpflichtet mich heirdurch noch zu ganz besonderem Dank.

"Ich wünsche der Chemical Society stets Wachsen und Gedeihen und bitte meiner auch fernerhin freundlich zu gedenken.

"Mit vorzüglicher Hochachtung,

"C. R. Fresenius."

Of the following papers those marked * were read:—

*1. "*Octacetylmaltose.*" By Arthur R. Ling and Julian L. Baker.

Octacetylmaltose, $C_{12}H_{14}(OC_2H_3O)_8O_3$, is obtained by boiling maltose with acetic anhydride and anhydrous sodium acetate (Liebermann's method). It crystallises from alcohol in magnificent long prismatic needles, melts at 158—159° without decomposing, is sparingly soluble in cold alcohol, readily so in benzene, glacial acetic acid, and hot alcohol, and extremely soluble in chloroform, but insoluble in water. Its specific rotatory power in chloroform is $[\alpha]_D = +62{\cdot}22$ (mean of two observations), and in alcohol (two observations) $[\alpha]_D = +59{\cdot}31$. No birotation was observed. The compound has no taste. Herzfeld (*Ber.*, xiii., 267; *Annalen*, ccxx., 215) has described an octacetylmaltose, prepared by the same method. He states that it crystallises from alcohol in colourless prisms, melting at 150—155°, but decomposing, that it has a bitter taste, is insoluble in chloroform, and has a specific rotatory power in alcohol $[\alpha]_D +81{\cdot}8$. The authors, therefore, conclude that Herzfeld's description of the compound is in many respects erroneous.

*2. "*Action of Diastase on Starch.*" By Arthur R. Ling and Julian L. Baker.

The authors have carried out numerous experiments in order to prove the existence or otherwise of Lintner's so-called isomaltose, which is said to be one of the products of the hydrolysis of starch (*Ber.*, xxvi., 2538). As the result of a study of the action of precipitated diastase (prepared from low-dried distillers' malt by Lintner's method) on starch, they have isolated a very hygroscopic substance having, roughly speaking, the same properties as Lintner's supposed compound, thus: $[\alpha]_D$ 143, and R (= per cent of maltose) = 81·5. This substance gave numbers on analysis agreeing with the formula $C_{12}H_{22}O_{11}$, and cryoscopic determinations seemed to point to this as the molecular formula. A microscopic examination of the substance showed, however, that it contained crystals resembling maltose, and it yielded nearly half its weight of octacetylmaltose on acetylation. Treated with diastase, the reducing-power was raised to R=94·6, but the sp. gr. of the solution before and after treatment remained unaltered, a point to which Hiepe has drawn attention. It was found to ferment but slowly with ordinary beer yeast, the unfermented residue being unaltered in properties. The osazone was separable into a large fraction melting at 182—185° which resembled maltosazone in appearance, and a very small fraction melting at 145—152°. The authors suggest tentatively, that the substance may possibly contain the simple dextrin $C_{12}H_{20}O_{10}+H_2O$, a view which derives some support from the fact that the sp. gr. of a solution remains unaltered after being submitted to the action of diastase.

When starch paste is treated at 70° with the diastase obtained from pale brewers' malt, which is dried at a much higher temperature than that manufactured for distillers, the alcoholic extract of the product yields, on treatment with phenylhydrazine, a small quantity of glucosazone, and an osazone which, when repeatedly recrystallised from hot water, has all the properties of Lintner's so-called isomaltosazone; thus, it crystallises in nodular groups of extremely minute yellow needles, and melts at 150—153°. On analysing this substance, it gave the numbers of a *triosazone*. The mean analytical values are found: C=52·73; H=6·20; N=8·31 per cent. The formula $C_{12}H_{20}O_9(N_2HC_6H_5)_2$ requires C = 52·78; H=6·15; N=8·21 per cent.

The authors therefore are inclined to conclude that a triose, $C_{18}H_{32}O_{16}$, is one of the products of the action of diastase on starch, and are now attempting its isolation.

Discussion.

Mr. Horace T. Brown expressed satisfaction that the question of the hydrolysis of starch was once more attracting the attention of English chemists The authors' recent work promised to be a valuable contribution to the subject. As the speaker and Dr. Morris are at the present time engaged in a thorough re-investition of the chemistry of starch hydrolysis, he could not say much about it on this occasion, but hoped to lay their results before the society at no far distant date.

It was satisfactory that the authors had been able to confirm the existence of the maltodextrin described by Dr. Morris and himself. It has recently been urged by Lintner that this is not a pure substance, but a mixture of his "isomaltose" with the dextrins; such, however, is not the fact. Whilst admitting that every credit is due to C. J. Lintner for first calling attention to the fact that amongst the products of starch hydrolysis there is a substance other than maltose, producing a definite and crystallisable osazone, there was no doubt in the speaker's mind that Lintner was mistaken both as to the constitution and properties of the substance in question, and he agreed so far with the authors that Lintner's isomaltose was not a chemical entity. He was not prepared, however to admit the triose nature of the substance yielding the osazone described, and could not regard the mere analysis of the osazone as a proof of this.

*3. "*New Derivatives from α-Dibromocamphor.*" By Martin O. Forster, Ph.D.

Among the many well-known peculiarities displayed by derivatives of camphor, is the fact that whilst monobromocamphor is readily acted on by somewhat dilute nitric acid, being in part converted into a nitro-derivative and in part oxidised to camphoric acid, α-dibromocamphor (m. p. 61°) is unaltered by acid of the strength which at once attacks the mono-derivative, although its conversion into monobromocamphor is readily effected by digestion with alcoholic potash. At Dr. Armstrong's suggestion the author has extended the study of dibromocamphor in the hope of explaining its relationship with monobromocamphor, and at the same time of throwing further light on the nature of camphor itself. The experiments form part of a comprehensive series now being carried on in the Central Technical College Laboratory with the object of investigating the behaviour of the substituted derivatives of camphor generally.

Whereas dilute nitric acid is without action on α-dibromocamphor, spontaneous development of heat is observed to attend its dissolution in the fuming acid (d. 1·52), the action culminating at about 70° in brisk evolution of red fumes. The chief product is a colourless solid, which crystallises from alcohol in long, prismatic needles melting at 152°. On analysis this has given the following results :—Carbon 36·86 and 36·95; hydrogen, 4·38 and 4·36; bromine, 49·13, 49·50, and 49·20, the values calculated for the formula $C_{10}H_{12}Br_2O_2$, being 37·03 carbon, 3·70 hydrogen, and 49·38 bromine, it seems probable that by the action of nitric acid two atoms of hydrogen in dibromocamphor are displaced by an atom of oxygen. The substance is neutral in character, and does not appear to be acted on either by phenylhydrazine or by hydroxylamine; hot sodium ethoxide converts it into a substance soluble in alkalis, which does not contain bromine.

When the solution of the new derivative in hot alcohol is digested with zinc dust and ammonia it is reduced. The product crystallises in thin, lustrous, hexagonal plates melting at 159°. On analysis it is found to contain 48·81 carbon, 6·08 hydrogen, 32·44 bromine; the values calculated for $C_{10}H_{13}BrO_2$ being 48·98 carbon, 5·30 hydrogen, 32 65 bromine. The compound has phenolic properties, and forms a dark green, crystalline copper salt, but remains unchanged when heated on the water bath with acetic anhydride and sodium acetate. Sodium ethoxide has no action on it; on treatment with bromine it is re-converted into the original dibromo-compound (m. p. 152°).

On adding fuming nitric acid to the solution of the monobromo-derivative in glacial acetic acid, the liquid acquires a green colour, and on warming it a violent action is set up, red fumes being evolved. In this way a nitro-derivative is obtained crystallising in colourless needles which melt at 125°, containing carbon, 40·82; hydrogen, 4·82; bromine, 29·70; nitrogen, 5·56. The values calculated for $C_9H_{12}BrO{\cdot}NO_2$ being 41·22 carbon, 4·58 hydrogen, 30·53 bromine, and 5·34 nitrogen, it appears that, simultaneously with nitration, elimination of a carbonyl group has taken place, a change which is in some respects comparable with the formation of sulphocamphylic acid from camphoric acid. When this nitro-compound is reduced in alcoholic solution with zinc dust and ammonia, bromine is eliminated, and a colourless nitrogenous substance is formed, crystallising from boiling water in lustrous laminæ which melt at 159—162°.

A remarkable feature of the change undergone by α-dibromocamphor in contact with fuming nitric acid, is the formation of a small quantity of ordinary monobromocamphor melting at 76°.

It is proposed to study the behaviour of other camphor derivatives, especially bromochlorocamphor and dichlorocamphor, towards nitric acid. From the former a new substance has already been obtained, together with monobromocamphor. The new product crystallises in fine silky needles melting at 143·5°; on reduction it yields a phenolic, monohaloïd derivative from which it may be reproduced by bromination. The description of these compounds is reserved for a later communication, together with the products of the sulphonation of α-dibromocamphor, which, it is found, may be effected without difficulty.

*4. "*Acid Sulphate of Hydroxylamine.*" By E. Divers, M.D., F.R.S.

The author has prepared crystalline hydroxylamine hydrogen sulphate, NH_2OH,H_2SO_4, by acting on solid hydroxylamine hydrochloride with the calculated quantity of sulphuric acid. When the first action is over, the product is heated during several hours at 100° to expel hydrogen chloride, and the cold viscid liquid left in a desiccator until it has set to a translucent mass of prismatic crystals. These, after drying on a porous tile, were analysed, and furnished results agreeing with those calculated from the formula.

*5. "*The Hypophosphites of Mercury and Bismuth.*" By S. Hada.

Attempts to prepare a mercurous hypophosphite were unsuccessful. By acting on a solution of mercuric or mercurous nitrate with potassium hypophosphite, a white, unstable precipitate of the double mercurous nitrate and hypophosphite, $HgH_2PO_2,HgNO_3,H_2O$, is obtained. This salt explodes when heated above 100°.

Bismuth Hypophosphite, $Bi(H_2PO_2)_3,H_2O$, is readily prepared by adding a solution of bismuth nitrate to a solution of potassium hypophosphite. It is a white, crystalline powder, which is fairly stable when dry. When strongly heated, this salt decomposes in accordance with the equation $3Bi(H_2PO_2)_3 = 2Bi + Bi(PO_3)_3 + 6P + 9H_2O$.

6. "*Kamala.*" Part II. By A. G. Perkin.

The three acids melting respectively at 282°, 226°, and 232°, produced by the action of nitric acid on rottlerine (*Trans.* 1893, 982), have been prepared in larger quantity and re-examined, with the result that they were found to contain nitrogen, and to consist of *ortho-* and *paranitrocinnamic* acids and *paranitrobenzoic acid*. *Paranitrobenzaldehyde* was also isolated from among the products of this action. Paranitrobenzoic acid, also obtained in a similar way from the resins of high and low melting points and isorottlerine (*Trans.*, 1893, 986, 989, 990), results evidently from the oxidation of the paranitrocinnamic acid which is first formed.

Crystalline metallic compounds of rottlerine have been prepared, having respectively the formulæ $C_{33}H_{29}O_9Na$, $C_{33}H_{29}O_9K$, $(C_{33}H_{29}O_9)_2Ba$, $(C_{33}H_{29}O_9)_2Pb$, and $C_{33}H_{29}O_9Ag$, showing that rottlerine must be represented as $C_{33}H_{30}O_9$, or three times the formula $C_{11}H_{10}O_3$ originally assigned to it by Anderson (*Edin. New. Phil. J.*, i., 300). These results point also to the probability that rottlerine is a monobasic acid, $C_{32}H_{29}O_7.COOH$.

When boiled with sodium carbonate solution rottlerine is decomposed, yielding, together with resinous products, a substance crystallising in garnet-coloured prisms, to which the formula $C_{29}H_{26}O_6$ has been provisionally assigned. It is insoluble in aqueous alkalis, except in presence of alcohol. For this substance the name *rottlerone* is proposed.

7. "*The Action of Aqueous Potassium Cyanide on Gold and Silver in presence of Oxygen.*" By J. S. Mac Laurin, B.Sc., University College, Auckland, New Zealand.

This is a continuation of a paper (*Trans.*, 1893, 724—738) in which the interaction of gold and potassium cyanide—the basis of the now extensively applied Mac Arthur-Forrest or Cassell process—was investigated.

Further results are quoted proving the necessity of oxygen. The rate of dissolution of gold in potassium cyanide solutions is re-investigated, and that of silver is also determined. The rate of dissolution increases as the concentration of the solution decreases, reaching a maximum when solutions containing 0·25 per cent are used, and then decreasing. It is also shown that the ratio of the gold dissolved by any given cyanide solution to that of the silver dissolved by the same solution is approximately the ratio of their atomic weights. The remarkable variations in the solubility of gold and silver may be explained by the fact that the solubility of oxygen in cyanide solutions decreases as the concentration increases, and that the solvent power of the strong solutions is thus rendered less than that of the weaker solutions which are capable of taking up more oxygen. The relations of the gold, silver, and oxygen dissolved are shown in a table under headings—

$$\frac{Au}{O} \text{ and } \frac{Ag}{O},$$

and it is pointed out that if the amount of gold or silver dissolved depend solely on the quantity of oxygen in solution, the values—

$$\frac{Au}{O} \text{ and } \frac{Ag}{O}$$

should be constant; actually these values gradually decrease as the concentration of the solution increases. Therefore in the more concentrated solutions there is less metal dissolved than the amount of oxygen in solution apparently demands. This points to some retarding action on the motion of the oxygen molecules. As it seemed probable that viscosity would have such a retarding action, the rates of dissolution of gold and silver were determined in cyanide solutions rendered more viscous by the addition of various substances, such as sugar and glycerol, which might be assumed to exert no chemical influence on the solubility of these metals. The results show that the assumption is correct. Moreover, the viscosity coefficients of cyanide solutions of varying strengths were determined, and the values—

$$\frac{Au}{O} \text{ and } \frac{Ag}{O}$$

were calculated by the aid of a formula previously given; these agree very closely with those found, showing that the rates of dissolution of gold and silver are proportional to the amount of oxygen in solution, and to the coefficient of viscosity.

8. "*The Crystalline Form of the Isomeric Dimethylpimelic Acids.*" By William J. Pope.

In order to obtain confirmatory evidence of the distinct nature of the two dimethylpimelic acids isolated by Dr. Kipping, a crystallographic examination of the two products was undertaken.

The acid melting at 81°—81·5°—paradimethylpimelic acid — crystallises on spontaneous evaporation of its aqueous solution in minute colourless rhombohedra belonging to the monosymmetric system, and showing the forms $c\ \{001\}$, $a\ \{100\}$, and $m\ \{110\}$; in one case a face of the form $p\ \{11\bar{1}\}$ was observed; $a : b : c = 1{\cdot}263 : 1 : 1{\cdot}062$. $\beta = 43° 23'$. It sometimes crystallises in flat rhomboidal plates showing the forms $c\ \{001\}$, $p\ \{11\bar{1}\}$, and $p'\ \{111\}$, which have the same crystalline form as the rhombohedra.

The acid melting at 76—76·5°—antidimethylpimelic acid—crystallises from its aqueous solution in small orthorhombic prisms showing the forms $m\ \{110\}$ and $p\ \{101\}$; $a : b : c = 0{\cdot}821 : 1 : 2{\cdot}862$. A well-defined orthorhombic interference figure of large axial angle is seen through the face p (101); the optic axial plane is parallel to b (010).

The crystallographic comparison of the two acids thus confirms their chemical dissimilarity in the most striking way.

9. "*Oxidising Action of Ammonia Solution on some Metals.*" By W. R. Hodgkinson and Lieut. N. E. Bellairs, R.A.

That an oxidation takes place when copper, moistened with ammonia solution, is placed in contact with air seems to be generally known (Schönbein, *Ber. Ak. B.*, 1856, 580; *J. B.*, lvi., 311; *Ann. Chim. Phys.*, [4], i., 381; Peligot, *Compt. Rend.*, xlvii., 1034).

Undoubtedly both copper and ammonia become oxidised in this case. As other metals dissolve to some extent in ammonia solution, the authors have determined whether any similar oxidation took place under ordinary conditions of temperature.

As might be expected, those metals which form soluble double salts with ammonium salts are most acted on by ammonia solution.

Zinc, nickel, and cobalt are, after copper, most rapidly attacked, a considerable amount of metal in each case being dissolved. Lead dissolves more slowly, and iron, magnesium, and aluminium do not appear to dissolve at all.

In the case of copper, the formation of nitrite is detectible after ten minutes' contact of the metal and ammonia in presence of air. To make a comparative test, the metals mentioned were exposed in small pieces to ammonia solution, and air in similar flasks covered only with watch-glasses during forty-eight hours. They were then examined for nitrite or nitrate by (1) potassium iodide, (2) ferrous sulphate, and (3) naphthylamine sulphanilic acid.

Zinc, nickel, lead, magnesium, aluminium, iron, and palladium in foil failed to form any nitrite.

The nickel was obtained from nickel carbonyl. After more than a week's exposure to the ammonia, although it formed a deep blue solution, no trace of nitrite was found. Cobalt, however, even after twelve hours, afforded a very appreciable amount of nitrite, the amount appearing to increase regularly with the time of exposure.

10. "*Action of Magnesium on some Phenylhydrazine Compounds.*" By W. R. Hodgkinson and A. H. Coote.

In a note to the Society (*Proc.*, cxxxvii., p. 80) the authors described very shortly the action of magnesium on phenylhydrazine.

This metal acts on the acid derivatives with less violence than on phenylhydrazine itself, but it is still energetic when the magnesium is employed in the form of filings.

Acetylphenylhydrazine, $C_6H_5NHNHCOCH_3$, melting at 128°, was mixed with magnesium filings and heated somewhat quickly in a retort to a little above its boiling-point; there was considerable frothing and evolution of gases, which proved to be hydrogen and nitrogen; the water over which they were collected contained much ammonia. Other products, condensed before reaching the water, were benzene, aniline, acetanilide, and ammonium acetate, with a little unchanged acetphenylhydrazine. The retort residue contained magnesium acetate, magnesium oxide, and some carbonaceous matter.

It seems probable that the first attack of the magnesium is on some of the acetyl groups, which thus furnish hydrogen, which, in turn, splits up other molecules of the acetylphenylhydrazine into aniline, benzene, &c.

The action is, therefore, somewhat different from that of the metal on phenylhydrazine.

Acetanilide, phthalanil, and several other anilides can be distilled over magnesium without appreciable action or change.

Benzoylphenylhydrazine behaves like the acetyl compound. The products of the action of magnesium are hydrogen, nitrogen, ammonia, benzene, aniline, and ammonium benzoate.

So far the amounts of *benzene*, *aniline*, and *acetanilide* obtained indicate that $4(C_6H_5NHNHCOCH_3)$ gives—

$$2(C_6H_5NH_2)+C_6H_6+C_6H_5NHCOCH_3+3NH_3\ ;$$

the other products are still undetermined.

11. "*Refraction Equivalents of the Elements and the Periodic Law.*" By R. M. Deeley.

In this paper it is shown that the refraction equivalents of the elements for the most part fall into line with the modified periodic arrangement of the elements, which the author has previously suggested (*Trans.*, 1894).

PHYSICAL SOCIETY.

Ordinary Meeting, January 25th, 1895.

Mr. Medley concluded the reading of a paper by Prof. Ayrton and himself on "*Tests of Glow-Lamps*," which was commenced at a former meeting.

With the newer lamps employed in these tests, it was found that candle-power, current, and candles per watt all rose as the lives of the lamps increased. The authors, being surprised at this result, took care to satisfy themselves that the effect observed was due neither to change in the resistance of their manganin potentiometer strip, nor to uncertainty of contact at the sockets of the lamps. Starting again with new lamps, they found that in all cases the light given out was greater after the lamps had been glowing for some time than it was when they were new. In the earlier tests a considerable falling off in candle power had always taken place after the lamps had been running for some time. Further, while the globes of the earlier lamps were always much blackened, even after a run of a few hundred hours, and so became comparatively useless long before the filament broke, the Edison-Swan lamps now examined showed hardly any blackening, even when the filaments lasted over 1300 hours. The rise in candle-power was always accompanied by a rise in current, which was, however, proportionately much smaller, so that the consumption of power per candle was actually less after the lamp had been running 50 hours than it was at the beginning. Among the conclusions drawn by the authors were the following:—(*a*) When a group of Edison-Swan lamps marked 100—8 are run at 100 volts, and each lamp as its filament breaks is replaced by a new one, it may be expected that the light given out will never subsequently be as small as when all the lamps were new; (*b*) an Edison-Swan lamp marked 100—8 when run at 100 volts, will give an average illumination of about ten candles, and will absorb on an average power of about 4·3 watts per candle, so that such a lamp must be regarded as a 43-watt lamp, and not a 30-watt lamp as is frequently stated; (*c*) the maximum rise of light recorded during the life of any lamp was 45 per cent; (*d*) with lamps of the type examined, there is no point at which it becomes economical to discard a lamp before its filament actually breaks; (*e*) no marked economy can be gained by over-running such lamps (*i.e.*, by using pressures exceeding 100 volts).

Professor Ayrton mentioned that the improvement in glow-lamps after running for some time had been attributed to an improvement in the vacuum. Experiments made on new and used lamps by means of an induction coil, showed that the more a lamp was used the better the vacuum became, but he (Prof. Ayrton), though at first inclined to adopt this explanation, had since found that, though in all the lamps examined, the progressive improvement of the vacuum was equally marked, the increase in candle power varied between very wide limits, being very considerable in some lamps and hardly perceptible in others.

Professor Rücker asked if it made any difference to the life of a lamp whether it were kept running continuously until the fibre broke, or were run for periods of a few hours, alternating with intervals of rest. The latter case would more nearly correspond with the conditions obtaining in practice.

Professor Ayrton replied that the lamps were kept running during the night, and were disconnected during the day.

A paper by Prof. Anderson and Mr. J. A. McClelland "*On the Temperature of Maximum Density of Water, and its Co-efficient of Expansion in the Neighbourhood of this Temperature*," was read by the secretary, Mr. Elder.

The dilatometer method was used, but the bulb of the instrument contained a quantity of mercury, determined by experiment, which for the range of temperature concerned was such as to secure the constancy of the remaining internal volume occupied by water. The observed changes were thus the real and not the apparent changes. The bulb was furnished with a graduated tube of small bore, bent twice at right angles, which served at the same time the purpose of a ground glass stopper. (The joint was made water-tight by a little Canada balsam). To determine the coefficient of expansion of the glass, the bulb and tube were fitted with mercury at 0° C., and heated up to about 9·7° C., the necessary weighings being afterwards performed. The coefficient of expansion of mercury being known, the number of grms. of mercury to be kept in the bulb during the experiments on water was calculated. The dilatometer was next filled with (thoroughly boiled) distilled water at about 8° C., the stopper end of the graduated tube inserted, and the free end dipped under mercury, giving at 4° C. a column of mercury whose changes of level could be observed. A thermometer was placed with its bulb close to the middle part of that of the dilatometer; both being immersed in a water-bath which could be cooled by the addition of ice-cold water, or cooled by radiation from surrounding objects. The thermometer used was graduated to tenths of a degree, and was compared with two similarly graduated ones by different makers. The two latter agreed very closely with one another, and one had a Kew certificate showing no error in the readings. Temperatures were written to the fourth decimal place, but accuracy to this extent was not claimed. Three sets of experiments were made, and for each a corresponding curve was drawn. In the first the water was at atmospheric pressure; in the other two at 1½ and 2 atmospheres respectively. Corresponding to these three pressures the temperatures of maximum density found were 4·1844° C., 4·1823°, and 4·1756°. The value 4·1844° corresponding to atmospheric pressure is greater than that generally received.

Mr. Rhodes thought that sufficient precaution had not been taken to accurately calibrate the thermometers. He doubted whether temperatures read in the manner described could be relied upon to much less than 0·1 degree. He did not see that any real advantage was gained by having mercury inside the dilatometer to compensate for the expansion of the glass.

Mr. W. **Watson** thought that the mercury within the vessel would cause further uncertainty by tending to produce distortion of the glass. He pointed out that in the case of water at maximum density, there would be practically no convection currents, so that equalisation of temperature would be very slow. As the bulb used was about 8 c.m. in diameter, and all the experiments were made with the temperature rising, he thought that this would account for the high value obtained for the temperature of maximum density.

Dr. **Burton** thought a distinct advantage was gained by compensating for the expansion of the glass. The values obtained in different experiments did not seem to be highly concordant.

Professor **Rücker** thought that the criticisms which had been passed were for the most part just. For such measurements as those recorded, it was not sufficient to know the corrections of the thermometer readings at a few isolated points; the portion of the stem over which the readings were taken must be carefully and minutely calibrated. The Kew certificate not only ignored errors of less than 0·05 degree (as mentioned by the authors), but it only gave corrections for a small number of temperatures, separated by considerable intervals.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

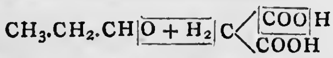
Dr. **Dobbin** in the chair.

The fifth meeting of the Society took place on the 28th January.

Dr. **Mackenzie**, of the Heriot-Watt College, read a paper on "*Unsaturated Fatty Acids.*"

By way of introduction, unsaturated acids were defined, and a short description of the nomenclature, general methods of preparation, and general properties was given. The methods of determining the constitution were more fully gone into. The method of fusion with potash was shown to give misleading results. The HBr and Br addition-products of the acids are characteristic. The αβ acids give β-bromacids, which on boiling with water yield unsaturated hydrocarbons, β-oxyacids, and a mixture of αβ- and βγ-acids. βγ-acids give γ bromacids, which on the same treatment yield γ-lactones. Similarly αβ-dibromacids give monobrom unsaturated hydrocarbons besides unsaturated monobrom and monobromoxyacids. From βγ-dibromacids result monobrom lactones. The method of boiling with dilute sulphuric acid determines quantitatively the proportions of αβ- and βγ-acids in a mixture. The former remain unchanged, the latter yield lactones. The conversion of βγ into αβ and oxyacids by boiling with dilute caustic soda was noted. For a concise yet comprehensive account of the subject, members were referred to Fittig's lecture "On Unsaturated Acids" (*Ber.*, xxvii., 2658). A short account of αβ-pentenic acid or propylideneacetic acid, $CH_3.CH_2.CH:CH.COOH$, was then given.

Komnenos (*Ann.*, cxviii., 166) first obtained, by the condensation of propionaldehyd and malonic acid with glacial acetic acid, a liquid of the empirical formula $C_5H_8O_2$ and b.-p. 194°—198°, which did not solidify in a freezing mixture. From its formation,—



$$CH_3.CH_2.CH\boxed{O + H_2}C\begin{matrix}\diagup \boxed{COO}H \\ \diagdown COOH\end{matrix}$$

he concluded it to be propylideneacetic acid, and this remained undisputed for some years.

Zincke and Küster (*Ber.*, xxii., 486), by reduction of a pentachloracid, obtained a liquid which they found identical with that of Komnenos. This they considered to be propylideneacetic acid, although its HBr addition-product gave a lactone on boiling with water, contrary to the general behaviour of αβ-acids. Two years later, Ott (*Ber.*, xxiv., 2600) described the separation of the Ba salt of Komnenos' acid into a part soluble and one insoluble in alcohol. From the re-crystallised insoluble salt he prepared an acid of b.-p. 193·5°. From another fraction of the insoluble salt he prepared βγ-pentenic acid (ethylidenepropionic acid) of b.-p. 193—194°. Dibromides of both acids were alike in m.-p. and crystallographic properties. Two years later, Viefhaus (*Ber.*, xxvi., 915) repeated Ott's work, but came to the conclusion that acid from the Ba salt soluble in alcohol was the αβ-acid, and that from the insoluble salt the βγ acid, because the former gave only 20 per cent, the latter 70 per cent lactone, on boiling with sulphuric acid. Evidently both acids were impure. The αβ-acid was at the time of Viefhaus' publication obtained pure by Fittig and Mackenzie. By partial separation by means of the Ba salt, and then boiling with sulphuric acid until no more lactone resulted, a liquid was obtained which boiled at 200°—201° without decomposition, and on cooling solidified to leafy crystals of m.-p. 9·5°—10·5°. The HBr and Br addition products were also got in crystalline form. The former yielded the products expected on boiling with water. In the same research it was found that by fractional crystallisation of the insoluble Ba salt, the βγ-acid was obtained pure. For further particulars members were referred to *Liebig's Annalen*, cclxxxiii, 82. In the last issue of the *Berichte* (xxvii., 3364), Zincke writes that on repeating his work, he finds the acid obtained by Küster and himself to be βγ-acid, and to contain no αβ-acid.

CORRESPONDENCE.

ARGON.

To the Editor of the Chemical News.

Sir,—In a paper recently communicated to the Chemical Society, I have shown that the refraction equivalents of the elements vary periodically with much regularity. The following tables show the nature of the variation for those elements with which argon must it seems be classed.

Element.	Atomic weight.	Refraction-equivalent
Carbon	12	5 or 6
Nitrogen	14	4·1
Oxygen	16	2·8 or 3·4
Fluorine	19	1·6
Argon	20 ?	?
Sodium	23	4·3
Magnesium	24·3	6·7
Aluminium	27	7·7
Or—		
Potassium	39	7·85
Calcium	40	10·0
Argon	40 ?	?
Scandium	44 ?	?
Titanium	48	24·0

From potassium to titanium the refraction-equivalent rises rapidly, the value for calcium being 10. If argon, like calcium, has an atomic weight of 40, we should expect to find its refraction-equivalent also about 10. On the other hand, if its atomic weight be 20, and it falls between fluorine and sodium, the refraction-equivalent might be 3 or even smaller than that of fluorine. For between carbon and aluminium the refraction-equivalents decrease rapidly until fluorine is reached. They then increase, with increasing atomic weight, and more than regain their original value at aluminium.

As the refraction-equivalent is calculated from—

$$P\frac{\mu - 1}{d};$$

P being the atomic weight, its value will depend upon the position assigned to the element on the atomic scale. Three and ten, however, not bearing the same ratio to each other as do twenty and forty, different refractive indexes are required for the two positions.

A determination of this physical constant would enable us to calculate the refraction-equivalent of argon, and the figure so obtained might point clearly to one of the possible values, 20 or 40, being the correct atomic weight of the new element.—I am, &c.,

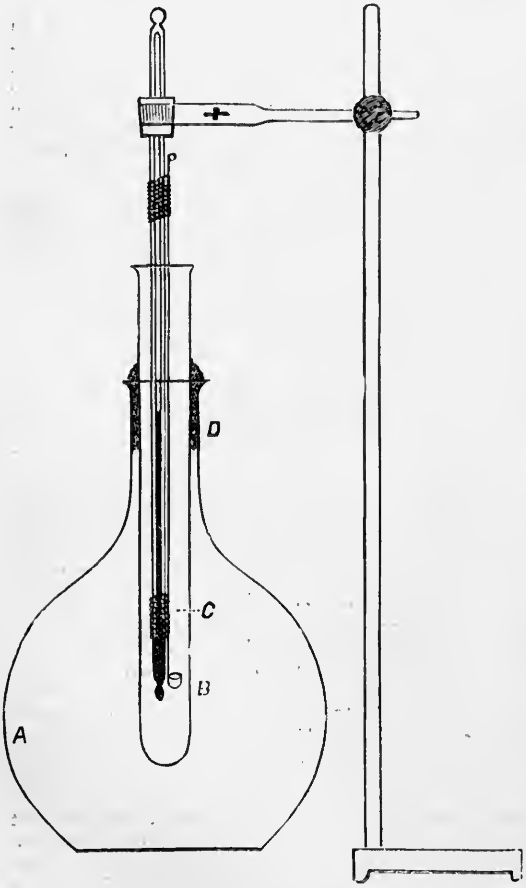
R. M. Deeley.

1, Charnwood Street, Derby,
February 2, 1895.

TAKING MELTING- AND IGNITING POINTS.

To the Editor of the Chemical News.

Sir,—The enclosed is a rough sketch of an apparatus I have employed in my classes for some years for taking melting-points and igniting-points of explosives.



A. 2-oz. flask.
B. Test-tube.
C. Thermometer with cup.
D. Asbestos packing.

For the latter a small platinum foil cup, about 2 m.m. wide and deep, is soldered to a platinum wire and suspended, as shown, close to the thermometer bulb and free in the centre of the test-tube. The outer flask (A) stands on two thicknesses of wire gauze, and is heated through this by the Bunsen flame so that a faint blue flame plays 2 or 3 c.m. high around the flask, and the wire gauze is scarcely red hot. Igniting point results are very satisfactory; for instance, nitroglycerine, four determinations, gave 158°, 157,° 158°, 157°.—I am, &c.,

W. R. Hodgkinson.

Artillery College.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 2, January 14, 1895.

Autumn Crops.—P. P. Dehérain.—The author has from time to time drawn attention to the considerable loss of nitrates undergone in autumn by soils after the removal of their crops, and insisted on the advantages of intermediate autumn crops. He now returns to the subject, showing that fields left bare lose weights of nitrates often greater than that applied in Spring as manure. This loss represents a sum equal to the rent of the land in a great part of France. He points out that in certain districts the soil is covered with an intermediate crop sown immediately after harvest and consisting by preference of leguminous plants.

Nomination.—The Academy proceeded to nominate a member of the Section of Mineralagy *vice* M. Mallard, deceased. The successful candidate was M. Hautefeuille.

Experimental Researches on the Critical-point of Liquids Holding Solids in Solution.—Raoul Pictet.—The author attempts to determine experimentally what is the solvent power of the vapours of liquids raised to a temperature above their critical-point. He finds that camphor is gaseous, or in a gaseous solution in the vapours of ether. Borneol remained totally dissolved in gases or in the vapours of ether. Guaiacol, phenol, and iodine behaved in a similar manner. Vapours of alcohol at 240° dissolve alizarin like liquid alcohol. The liquefaction of vapours presents two distinct phases: the one at temperatures above the critical-point, in a multitude of points at the centre of the vapours, the number of which is proportional to the pressure; the other phase is below the critical-point at the pressure of saturated vapours. Solids, on the contrary, dissolve in the total of the liquid vesicles disseminated among the vapours under a high pressure near the critical-point.

Certain Properties of Silver Sulphide.—A. Ditte.

Preparation of Amorphous Silicon.—M. Vigouroux.

Protomorphic Condition.—A. Villiers.

Certain Sensitive Reactions of the Amidobenzoic Acids.—Oechsner de Coninck.—These four papers will be inserted *in extenso* as early as possible.

A Class of Nitriles.—Albert Colson.—The ethers of the cyanals resist heat, but in contrast to the cyanic ethers they easily give off the elements of hydrocyanic acid. The author is about to examine if insoluble cyanic ether is or is not connected with the cyanals.

Constitution of Hexamethylentetramine.—R. Cambier and A. Brochat.—Methylenamidoacetonitrile is to hydrocyanic acid what hexamethylenamine is to ammonia.

Ethylenic Methylal.—L. Henry.—Not adapted for useful abstraction.

New Researches on Pectase and Pectic Fermentation.—G. Bertrand and A. Mallèvre.—We may conclude from these new researches that pectase exists in the cellular juice of acid fruits as in that of the roots of carrots. There is no insoluble pectase. But in the juice of acid fruits the presence of the ferment may be masked by the acidity of the medium, and its action then appears only on neutralisation.

No. 3, January 21.

On Boron Steel.—H. Moissan and G. Charpy.—The study of a compound of iron with small proportions of boron presents much interest, both from a practical and a theoretical point of view. The analogies existing between carbon and boron, and the difference of their atomic volume, render these experiments interesting as throwing a light on the constitution of steels. The authors have prepared an ingot of iron containing—

Boron	0·580
Carbon	0·17
Manganese	0·30
Silicon, phosphorus, sulphur	traces.

This alloy was rolled into a cylindrical bar, and it is easily forged at a dark-red heat; in a general manner it works like mild steel. Boron communicates to iron the property of taking a temper, but a special temper corresponding to an increase of the breaking strain without any appreciable augmentation of hardness. Its *rôle* is therefore quite distinct from that of carbon.

Nominations.—The Academy proceeded to nominate a correspondent for the Section of Medicine and Surgery, *vice* the late M. Pollet. M. Herrgott obtained an absolute majority of votes. The Academy next appointed a Commission to draw up a list of candidates for the rank of Foreign Associate, *vice* the late Herr Kummer.

Influence of Temperature on the Transformation of Amorphous Zinc Sulphide. — A. Villiers. — The temperature of transformation is not fixed for one and the same substance. It depends on the medium in which the substance exists at the moment of its formation, and also on the conditions which this medium has subsequently undergone. The temperature is very different for different media. It may be near zero or above 100°, according to the composition of the liquid and the variations of this composition during and after the precipitation of the zinc sulphide.

Insufficiency of Kjeldahl's Method for Determining Nitrogen in the Chloroplatinates. — M. Delépine.—In determining by this method the nitrogen in trimethylamine chloroplatinate the anthor found only 3·88 of nitrogen instead of the calculated quantity of 5·15 per cent. In a specimen of ammonium chloroplatinate he observed only 1·89 per cent in place of 6·26. This deficiency seems due to the action of the chlorine of the platinum chloride upon the ammonia, and doubtless upon the amine.

Upon Arabinochloral and Xylochloral.— M. Hanriot. — The author has previously shown that glucose may combine with chloral forming two isomers, the glucochlorals. He now seeks to generalise this reaction by extending it to other sugar. Arabinochloral answers to the formula $C_7H_9Cl_3O_5$. It is slightly soluble in cold water and chloroform, fairly soluble in heat in alcohol, ether, and benzene. Its rotatory power is $[\alpha]_D = -23{\cdot}2°$. With various reagents it behaves like β-glucochloral, though with orcine hydrochlorate it gives a blue colour. Xylochloral crystallises in laminæ fusible at 132°, being in part volatilised before fusion. It is much more soluble in water than arabinochloral. Its rotatory power is $[\alpha]_D = -13{\cdot}6°$. With orcine hydrochlorate it gives the same blue colour as does arabinochloral.

New Synthesis of Anthracene.—M. Delacre.—The author treated benzyl trichloracetate with benzene in presence of aluminium chloride and under the influence of heat. Instead of triphenylethane he obtained exclusively anthracene, which, after a single re-crystallisation, was perfectly pure.

A Contribution to the Study of the Tartaric Ethers.—Ph. A. Guye and J. Fayollot. — The ethers derived from the ethyl or isobutyl dextro-tartrate with a simple acid radicle are characterised by positive rotatory powers, algebraically inferior to that of the non-substituted tartrate. A full exposition of the author's views is not practicable without the accompanying diagrams.

Archives Néerlandaises des Sciences Exactes et Naturelles.
Vol. xxviii., Parts 3 and 4.

Emission of Oxygen under the Influence of Light by the Chromophyllic Cellules Demonstrated by the Bacterian Method.—Th. W. Engelmann.—The principal facts established in the author's beautiful researches are:—1. The green vegetable cells have the power of emitting oxygen in the light. 2. The intensity of this emission increases within wide limits with the intensity of the illumination. 3. The emission of oxygen begins immediately with the action of light, and ceases at the moment when darkness sets in. 4. The bacteria employed (principally *Bacterium termo*) require every instant free oxygen in order to move. 5. The rapidity of their movements increases to a large extent with the tension of the oxygen. 6. If the tension of the oxygen falls below a certain value, the movements cease at once; but they are resumed as soon as the tension is again increased. 7. The direction of the movements of the locomotion of the bacteria is influenced by the distribution of the tensions of the oxygen in the drop of liquid, chimiotaxis. The bacteria accumulate where the tension is greatest. Some species, however, such as *Vibrio lineola*, *Spirillum tenue*, &c., adapted to very low tensions of oxygen, accumulate when the tension is low in consequence of a feeble illumination. The red rays of light which are preferentially absorbed by chlorophyll determine an exceptionally strong emission of oxygen. The paper is illustrated with beautifully coloured plates, designed by the author, which are in fact necessary for his results. There is also appended a valuable bibliography of the subject.

MISCELLANEOUS.

The Name "Argon."—A valued correspondent sends us the following remarks on the origin of the name Argon:—"The root 'arg' in the name now appropriated to the new element has been employed before in a similar sense in the classification of molecules in steam into argules and ergules in Mr. Macfarlane Gray's paper on the 'Rationalisation of Regnault's Experiments on Steam.' It may be interesting to refer to the words of Jesus Christ, from which 'argule' was derived, 'Why stand ye here all day argoil.' It is this word 'idle' which appears again in the new name Argon, and the words of Jesus Christ are just what every chemist is to-day saying in regard to the new substance. The *Daily Telegraph*, in an able article on the new element, falls into a very amusing error. After remarking on the quietness of nitrogen in the atmosphere, it says 'Gentle nitrogen prevents all this; but try it in nitroglycerine, and how different its behaviour!' not knowing that it plays the same *rôle* in nitroglycerine as in the atmosphere. Nitrogen keeps the oxygen off the hydrogen and the carbon in nitroglycerine, and it is not until its pacific efforts have been overpowered by a surrounding disturbance, and when it has ceased to be nitroglycerine, that explosion occurs. In the explosion, however, the nitrogen merely walks off as if regretting that its efforts have been at last frustrated, and that these elements it had been keeping apart have in spite of it got foul of each other."

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.

Bichromates.—A correspondent asks for references to the best information on the manufacture of bichromates of potash and soda.

Purification of Water for Steam Boilers.—A correspondent asks where he can find detailed information on the subject of water purification, especially in relation to steam boilers.

MEETINGS FOR THE WEEK.

Monday, 11th.—Society of Arts, 4. (Cantor Lectures). "Means for Verifying Ancient Embroideries and Laces," by Alan S. Cole.
— Medical, 8.30.
Tuesday, 12th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Medical and Chirurgical, 8.30.
— Institute of Civil Engineers, 8.
— Photographic, 8. (Anniversary).
Wednesday, 13th.—Society of Arts, 8. "Light Railways," by W. M, Acworth.
— Pharmaceutical, 8.30.
Thursday, 14th.—Royal, 4 30.
— Society of Arts, 4.30. "Village Communities in Southern India," by C. Krishna Menon.
— Royal Institution, 3. "Meteorites," by L. Fletcher, M.A., F.R.S.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
Friday, 15th.—Royal Institution, 9. "Mountaineering," by Clinton T. Dent, F R.C.S.
— Geological, 3. (Anniversary).
— Quekett Club, 8. (Anniversary).
Saturday, 16th.—Royal Institution, 3. "English Country Songs" (with musical illustrations), by Sir Alexander Campbell Mackenzie, Mus. Doc.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1838.

SOME REMARKS ON "ARGON."

By BOHUSLAV BRAUNER, Ph.D.

I have read with great interest the contents of your "Argon" number of the Chemical News (vol. lxxi., p. 51), which has just reached me, and which contains the results of the classical researches of Lord Rayleigh and Professor Ramsay, Crookes, and Olszewski on that new gaseous constituent of our atmosphere.

When about two years ago I read for the first time the result of the work of Lord Rayleigh, who found that "chemical" nitrogen has a smaller density than "atmospheric" nitrogen, it struck me that this interesting fact might be explained by assuming that either "chemical" nitrogen consisted to a small extent of molecules dissociated into atoms, or that "atmospheric" nitrogen consisted partly of larger groups of atoms, *i.e.*, contained a polymeric form of nitrogen. If we compare the "volume weights" of (*a*) "chemical" nitrogen, (*b*) "normal" nitrogen, as calculated from its atomic weight, and (*c*) "atmospheric" nitrogen, we have—

$$a : b : c = 13{\cdot}995 : 14{\cdot}045 : 14{\cdot}067,$$

and it is seen that both hypotheses may be true at the same time.

We must consider that "chemical" nitrogen has been only a short time ago liberated all in free atoms, and these nearly completely united to molecules, so that it contains for 996·5 molecules N_2 *seven atoms N*, as calculated from the above numbers.

On the other hand, "atmospheric" nitrogen is as old as creation, and in this long time not only the originally free atoms might have completely united to molecules, but by some unknown reason larger atomic complexes might have been formed.

I was therefore surprised to find that in the paper read and in the following discussion the hypothesis, brought out originally by Dewar, *i.e.*, that "argon" is a kind of "nitrogen-ozone," a larger group of nitrogen atoms, N_3, was neither mentioned nor discussed, for it is striking that the density of such a gas would be exactly $d = 21$, whereas the highest value found by Rayleigh and Ramsay is $d = 20{\cdot}3$. There is a very powerful argument which speaks against the assumption that the gas is N_3, *i.e.*, the ratio of the specific heats at constant pressure to that at constant volume. I do not know whether this argument is so absolutely decisive as to make thoroughly useless any research in the direction whether the gas may still not be N_3.

Mendeleeff has shown that elements possessing a large atomic volume (in the solid state) combine easily with others, and explains this fact by assuming a comparatively large distance between the single atoms in the molecule (*e.g.*, Cs, vol. = 70), whereas elements which do not combine easily have a small atomic volume, *i.e.*, the atoms are very near each other (*e.g.*, the platinum metals, vol. = 8·3—9·2).

Though "argon" is a gas, a similar assumption of atoms lying very close to each other in the molecule would explain its great inertia, and such a close complex of three nitrogen atoms, weighing only 42, and showing no internal work, might be assumed to behave *physically* like a single atom.

The discoverers have tried several ways to induce chemical combination of argon, but as the gas seems to have been formed under conditions where other bodies decompose, it is very improbable that it will combine with other bodies under such conditions, and in fact it resists high temperatures and takes no part in reactions which are very energetic.

We have another source of powerful energy, viz., micro-organisms. We know micro-organisms which produce hydrogen arsenide from arsenic oxides; other micro-organisms convert ammonia into nitric acid, and some chemists think that they assimilate free nitrogen from the atmosphere; and last, not least, we know micro-organisms which reduce sodium carbonate to carbon monoxide. Is it not possible that such a source might have some action upon "argon"?

The most powerful source of chemical energy which is of a similar fermentative nature is nascent hydrogen liberated on contact of metallic palladium, or better rhodium, with formic acid. This thought was suggested to me by my friend Professor Rayman, who has been working in similar directions. If argon consist of polymeric nitrogen, it is probable that upon dropping formic acid upon rhodium in an atmosphere of argon, substances of the nature of hydrogen might be formed.

As an orthodox Mendeleeffian, I find great difficulty in assuming the existence of a new elementary gas having the atomic weight 20 or 40 or 80, its boiling-point being −187°. This low boiling-point would better correspond with a gas similar in its nature to nitrogen. On comparing, however, the boiling-points of O_2 and O_3 with that of N_2 and A, we find—

$$O_2 \;..\; -182{\cdot}7^\circ \qquad O_3 \;..\; -106^\circ \quad (d = 76{\cdot}7^\circ)$$

whereas—

$$N_2 \;..\; -194{\cdot}4^\circ \qquad A \;..\; -137^\circ \quad (d = 7{\cdot}4^\circ)$$

The difference between the boiling-point of oxygen and ozone is 76·7°, whereas that between nitrogen and argon is only 7·4° (*i.e.*, only the tenth of the former, so that in this case we have not the expected analogy).*

Again, the density of argon in the liquid state is about 1·5. The atomic volume,—

$$\frac{20}{1{\cdot}5} = 13{\cdot}3 \qquad \frac{40}{1{\cdot}5} = 26{\cdot}6,$$

and it is interesting to see that both these numbers find their place on the well known Lothar Meyer's curve of atomic volumes (ascending parts), *i.e.*, the atomic volumes agree well with the values expected for elements having the atomic weights either 20 or 40, and lying either between F = 19 and Na = 23, or between Cl = 35·5 and K = 39·1.

On reading very carefully the account of the discovery and the properties of argon one is struck by its great relation with nitrogen, and, in fact, the only observation which speaks against the assumption of an allotropic form of that element is of a purely physical character. We must not forget that it is contained in air to the amount of about one per cent, and that it therefore most probably plays an important *rôle* in nature and in life. We breathe 1 c.c. of argon for every 21 c.c. of oxygen, and I think that such a quantity of any other other substance but allotropic nitrogen would be hardly indifferent to our life.

Bohemian University, Prague,
February 6, 1895.

Solution of Solids in Vapours.—P. Villard.—The author states that the results obtained by Raoul Pictet (*C. R.*, Jan. 14, 1895) present a close agreement with his own relating to iodine dissolved in carbonic anhydride (*Journal de Physique*, Series 3, vol. iii., Oct., 1891). He adds that the absorption spectra in his observations, whether of the liquid or the vapour, presented in no case the flutings characteristic of gaseous iodine. Hence the latter seemed to be in a state of true solution in the vapour, even if not saturated.—*Compt. Rend.*, cxx., No. 4.

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* This want of analogy is not surprising on considering that the constitution of N_3 would very much differ from that of O_3, the latter being an endothermic very active substance. That the group N_3 *is* really differently constituted from O_3, is seen in the case of azoimide, N_3H, whereas we do not know any O_3H.

THE NASCENT STATE.

By LAUNCELOT ANDREWS, Ph.D.

I.

Mr. Joshua C. Gregory, in a recent number of the Chemical News (lxx., p. 188), criticises my previously published views on the nascent state as being too sweeping, and finds that I have "not succeeded in disproving nascent action." *That* I am quite ready to admit. All I hope to do is to show the inadequacy and the unnecessary character of the theory in a certain number of typical cases which have hitherto constituted the basis upon which the theory rested, and Mr. Gregory's objections give me a desired opportunity to record new observations bearing upon the disputed point.

He says "How else can the bleaching action of chlorine be explained? We know that moisture is necessary for this; we know that the action of chlorine is to set free oxygen; and we know, further, that this latter oxidises the colouring matter." Surely here is a sad confusion of knowledge with hypothesis!

What are the real facts with regard to the action of chlorine upon vegetable colouring matter. A solution of, say, indigo sulphuric acid in water is readily bleached by chlorine, while a piece of paper stained with the same solution, and then thoroughly dried, will withstand the action of the dried gas for a long time without visible change. This is the familiar experiment which, perhaps, Mr. Gregory had in mind in making the rather sweeping statement quoted, and which, in fact, has usually been interpreted as he interprets it.

Why is it not simpler to assume that the chlorine destroys the colouring matter by combining with its hydrogen to form hydrochloric acid gas? Two reasonable explanations can be given of the fact that the action takes place far more readily and quickly when the indigo is dissolved in water than when it is in the dry and solid form. These are—1st, the energy set free by the solution of the hydrochloric acid in the water goes to maintain the reaction (Berthelot's principle); 2nd, the failure to bleach in the second case may be due to the indigo being in the solid state, in which condition, as is well known, all reactions take place more slowly. Thus each particle of the colouring matter may well be supposed to soon become coated, in the absence of a solvent, with its own decomposition products, and so protected against further access of chlorine.

In order to test the admissibility of the second explanation, it is only necessary to dissolve indigo in a dry solvent free from oxygen, and to treat the solution with dry chlorine. If, under these conditions, the blue colour is not destroyed, the explanation just given must be faulty; but, on the other hand, if bleaching occurs, the explanation of Mr. Gregory, and with it the applicability of the nascent state hypothesis to this phenomenon, must be abandoned.

Experiment 1.—The attempt was made at first to dry a solution of indigo in chloroform with phosphoric anhydride, but this failed because the indigo gradually left the solution to combine with the phosphoric anhydride, the former becoming colourless. It was therefore necessary to dry the materials separately.

A small quantity of pure indigotin was exposed for a week in a desiccator charged freshly with phosphoric anhydride (P_2O_5). At the same time chloroform was dried by standing in contact with a quantity of the same material, the action being aided by occasional shaking. The chloroform was poured off into a well-stoppered bottle, the indigotin added, and a saturated solution of the latter in the former prepared by digestion. Some of the clear solution was then removed, and to it was added a dilute solution of bromine in chloroform which had been dried over P_2O_5 as described. Prompt bleaching ensued, the action being apparently no less rapid than in aqueous solutions.

Experiment 2.—Some of the solution of indigotin in chloroform, which had been dried as described, was treated with chlorine gas which had first passed a calcium chloride tower and then a phosphoric anhydride tube. The solution was very rapidly bleached.

From these experiments the only conclusion to be drawn is that, contrary to the general belief and to Mr. Gregory's explicit statement, *the presence of moisture is not a necessary condition to the bleaching of organic colouring matters by the halogens.* Probably the presence of *any* solvent for either the chlorine or the indigo would suffice.

II.

The reactions in which nitric acid is reduced to ammonia by the metals are exceedingly complex. It is therefore difficult to prove directly exactly what the steps are which do take place. Therefore many will doubtless prefer to adhere to the "nascent state explanation" until further investigation elucidates every step. For my part, it does not seem scientific to assume that nascent hydrogen is the active agent in the production of ammonia from nitric acid by the action of tin and hydrochloric acid, when it is a fact that stannous chloride alone is capable of quantitatively reducing nitric acid to ammonia,* the presence of nascent hydrogen being in the latter case impossible.

It would rather seem more logical to admit that, if in *any* case nitric acid can be reduced to ammonia without the presence of nascent hydrogen, the assumption of the latter as efficient cause of the reduction is needless in *all*. In order to gain further insight into the production of ammonia from oxidised compounds of nitrogen by reactions in which no hydrogen is set free, the following experiments were tried.

Experiment 3.—Crystallised stannous chloride (5 grms.) was dissolved in a large excess of a 20 per cent solution of sodium hydrate, and pure potassium nitrate (3 grms.) was dissolved in another portion of the same solvent. Both solutions were boiled in flasks provided with condensers, until the distillate no longer gave a reaction with Nessler's reagent; ammonia free distilled water, specially prepared for the purpose, being added from time to time to keep the bulk of the liquid from being too much diminished. Then the liquids were mixed and the distillation continued. The distillate, on Nesslerisation, showed no trace of ammonia.

Hence, nitrates are not reduced to ammonia by stannous hydrate in the presence of a large excess of caustic soda. This result was a surprise to me, although it should not have been, in view of the well-known great stability of the alkali nitrates at moderate temperatures. It was then argued that the less stable nitrates would be more likely to suffer reduction.

Experiment 4.—This experiment was conducted exactly like the last, except that one-tenth of a grm. of sodium nitrite was substituted for the same amount of potassium nitrate. The alkaline solutions of the nitrite and of the stannous hydrate, having been freed from every trace of ammonia, as described above, on being mixed and boiled evolved ammonia abundantly, the reduction being apparently quantitative.†

We see, therefore, that ammonia may be formed from nitric acid in acid solution by the reducing action of $SnCl_2$, and from nitrites in alkaline solution by $Sn(OH)_2$. In both cases there is no room for the assumption of nascent hydrogen, and the logical conclusion is that some explanation not involving this hypothesis and broad enough to cover all cases may and must be found. I do not think that there is at present quite enough foundation in known fact to build any theory upon, except in a suggestive and merely tentative way. In this spirit it may

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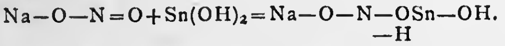
* Pugh, *Chem. Soc. Quarterly Journal*, xii, 35, abstract in *Jahresberichte*, 1859, 672.

† It is thought possible that a quantitative method for the separation of nitrites from nitrates, and for the determination of the former, can be based upon this reaction.

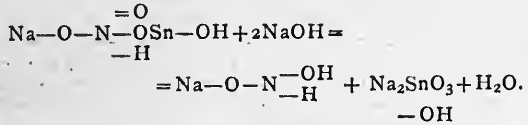
not be premature to point out that an analogy appears to exist between the so-called catalytic action, on the one hand, of aluminium chloride in inducing many organic syntheses, or of ferric chloride in promoting the formation of many chlorination or bromination products of organic compounds, and, on the other hand, of certain metals and of their salts in favouring the formation of ammonia from nitrous and nitric acids, and of sodium in forming highly hydrogenated products in presence of water or the alcohols.

In all these cases we have to assume the first step to consist in the formation of an addition product, the second in a reaction, of ordinary metathetic character, between the addition compound and one of the other bodies present. Such has been proved to be the true explanation of the remarkable activity of aluminium chloride. Such is probably accepted by most chemists already as the best explanation of the catalytic action of ferric chloride, and I would simply extend the explanation to cover all cases of so-called nascent action. For example, the reduction of the naphthylamines to dianoltetrahydronaphthylamines by sodium in the presence of boiling amyl alcohol would be conceived in accordance with the theory to consist in the formation of sodionaphthylamines, and in a subsequent reaction between these and the amyl alcohol, producing sodium amylate and hydronaphthylamines. Just what the addition products are, which this theory supposes to exist (for a brief moment), we cannot say, and most of them will probably defy efforts at isolation in consequence of their essentially evanescent and unstable character; but others we may well hope to discover, if we will only look for them. The close analogy of many are already known and isolated.

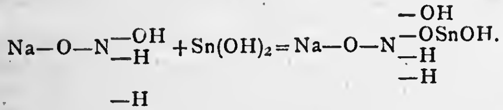
It may not be without interest to point out the application of this theory to the explanation of the reduction of sodium nitrite by means of stannous hydrate. We would assume:—

1. 

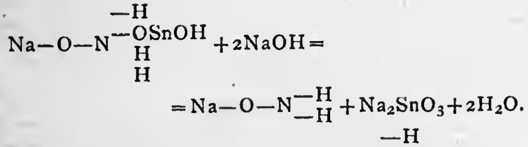
$$\mathrm{Na{-}O{-}N{=}O+Sn(OH)_2=Na{-}O{-}N}\begin{array}{l}\mathrm{=O}\\ \mathrm{-OSn{-}OH.}\\ \mathrm{-H}\end{array}$$

2. 

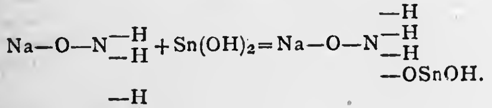
$$\mathrm{Na{-}O{-}N}\begin{array}{l}\mathrm{=O}\\ \mathrm{-OSn{-}OH}\\ \mathrm{-H}\end{array}\mathrm{+2NaOH=}$$
$$\mathrm{=Na{-}O{-}N}\begin{array}{l}\mathrm{-OH}\\ \mathrm{-H}\end{array}\mathrm{+\ Na_2SnO_3+H_2O.}$$

3. 

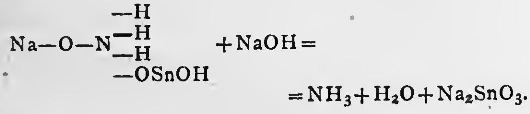
$$\mathrm{Na{-}O{-}N}\begin{array}{l}\mathrm{-OH}\\ \mathrm{-H}\end{array}\mathrm{+Sn(OH)_2=Na{-}O{-}N}\begin{array}{l}\mathrm{-OH}\\ \mathrm{-OSnOH.}\\ \mathrm{-H}\\ \mathrm{-H}\end{array}$$

4. 

$$\mathrm{Na{-}O{-}N}\begin{array}{l}\mathrm{-H}\\ \mathrm{-OSnOH}\\ \mathrm{\ H}\\ \mathrm{\ H}\end{array}\mathrm{+2NaOH=}$$
$$\mathrm{=Na{-}O{-}N}\begin{array}{l}\mathrm{-H}\\ \mathrm{-H}\end{array}\mathrm{+Na_2SnO_3+2H_2O.}$$

5. 

$$\mathrm{Na{-}O{-}N}\begin{array}{l}\mathrm{-H}\\ \mathrm{-H}\end{array}\mathrm{+Sn(OH)_2=Na{-}O{-}N}\begin{array}{l}\mathrm{-H}\\ \mathrm{-H}\\ \mathrm{-H}\\ \mathrm{-OSnOH.}\end{array}$$

6. 

$$\mathrm{Na{-}O{-}N}\begin{array}{l}\mathrm{-H}\\ \mathrm{-H}\\ \mathrm{-H}\\ \mathrm{-OSnOH}\end{array}\mathrm{+NaOH=}$$
$$\mathrm{=NH_3+H_2O+Na_2SnO_3.}$$

Of course, two equations instead of six would have been sufficient to make clear the leading idea, but I have preferred to employ the more complicated form because it is clearer to the mind, also because it better illustrates the progressive character of the reduction, and shows the intermediate products to be expected, any one of which may perhaps be isolated.

In concluding, I must not fail to point out that the view of Professor Smithells, which Mr. Gregory cites, stands in no necessary relation with the hypothesis of a nascent state, and many will be held as true even if the latter be discarded. It is undoubtedly true that it is often desirable to express in two equations a reaction which in fact takes place only in one stage. The value of a theory lies chiefly in its fruitfulness or in the power of prediction which it gives. The nascent state hypothesis could never have predicted the formation of ammonia from sodium nitrite by stannous hydrate, a prediction which constitutes the first fruit of the addition theory.

State University of Iowa,
Chemical Laboratory, January 18, 1895.

ON THE ACTION OF REDUCING AGENTS ON NICKELO-POTASSIC CYANIDE. MAGNETIC OXIDE OF NICKEL.

By THOMAS MOORE.

A continuation of the experiments (Chemical News, lxvii., p. 295) on this subject showed that the red solution could be produced by other means than by sodium amalgam; for example, zinc with a coating of either silver or copper acts very powerfully; it is also produced when a solution of the double cyanide containing an excess of alkali is electrolysed, the cathode being mercury. Many attempts were made to isolate the precipitate which the red solution gives with hydrochloric acid, but without success, as it rapidly decomposes whilst drying, with evolution of hydrogen. It is equally useless to try to obtain the oxide by the addition of oxycyanide of mercury, as instant decomposition takes place into metallic mercury and green oxide of nickel.

On considering what might be the action of potassium on the double cyanide, it was evident that, should a lower cyanide be actually formed, a certain amount of potassic cyanide should be set free, according to the eqnation—

$$3(\mathrm{NiCy_2 2KCy})+4\mathrm{K}=\mathrm{Ni_3Cy_2}+10\mathrm{KCy}.$$

Now it had been already noticed that solutions containing an excess of free KCy were the least suitable for the production of the red colour. It was therefore supposed that if this free KCy could be removed the stability might be increased. This end was attained by the further addition of nickel sulphate to the solution under reduction, this forming another portion of $\mathrm{NiCy_2 2KCy}$, which in its turn would be reduced with the formation of free cyanide. The operation is thus progressive. By proceeding in this manner more concentrated solutions can be obtained, but care must be exercised that the reduction is not pushed too far, as at a certain point the mercury commences to swell up after the manner of the ammonium amalgam, and the solution is rendered impure with little floating globules of mercury. There still remained, however, the task of precipitating the oxide, the isolation of the cyanide having been found to be surrounded by too many difficulties. This was accomplished by simply boiling the red liquor with ammonic chloride, and in this way getting rid of all cyanogen as volatile ammonic cyanide.

On boiling the properly prepared solution (that is, one containing little or no free KCy) with ammonic chloride in a non-oxidising atmosphere, a black precipitate is formed. This is washed several times by decantation, first with hot water and then with boiling dilute ammonia to which a little ammonic chloride has been added. This is repeated until the washings are free from nickel. Finally the precipitate is freed from ammonic chloride by repeated treatment with distilled water. By this means the precipitate is freed from all cyanide and oxide of nickel, and may now be dried on the filter paper at 100° C.; but it is preferable to detach the partly dried substance from the paper and continue the drying in a capsule, otherwise it adheres so forcibly to the filter and contracts so much during the process that it becomes contaminated with the fibre. Thus prepared the substance is obtained as a heavy black mass, which is apparently unaltered by exposure to the air at ordinary temperatures. It is easily soluble in sulphuric or hydrochloric acid with evolution of hydrogen, and also in nitric acids, whereby ruddy fumes are given off. In each case the ordinary green nickel salts are formed.

Carbon monoxide is without any action upon it. It is soluble in potassic cyanide, hydrogen being liberated. If the solution takes place in a non-oxidising atmosphere and with excess of alkali, the red cyanide is partially reproduced. It is also powerfully magnetic, being strongly attracted by a magnet. Tested qualitatively it gave no trace of cyanogen. Up to the present I have not succeeded in preparing it in a state of purity, as during the reduction the glass vessels are attacked by the alkali, in consequence of which the preparation contains some silica, &c.; nevertheless it is of sufficient purity for its composition to be determined. This was done by acting on the substance with a neutral solution of argentic nitrate. Decomposition begins at once and metallic silver separates out, often in brilliant spangles. On completion of the reaction (twenty-four hours) the precipitate may be filtered off and washed first with water and then with hot dilute sulphuric acid; the metallic silver and dissolved nickel may then be estimated in the usual way. Separate portions were taken for the estimation of impurities and water of combination; the latter had to be carried out in a combustion tube, catching up the water in calcium chloride tubes, owing to the oxidation of the precipitate at elevated temperatures. Many analyses were made, but one will suffice, as they are all very similar.

Weight of substance taken, 0·5974 grm.

	Found.
Ni	0·4251 grm.
H_2O	0·0958 „
SiO_2	0·0350 „
Alkali, &c.	0·0021 „
Oxygen (diff.)	0·0394 „
Silver reduced	1·0450 „

A quantity of gelatinous silica dried under similar circumstances gave on ignition slightly over 10 per cent water, so that it is safe to assume that the silica contained in the substance contained approximately this amount of water. If, therefore, the impurities and this water be deducted, the following is the percentage composition:—

	Found.	Theory for M_3ONH_2O.
Ni	76·34	77·20
O	7·08	7·01
H_2O	16·57	15·78

Again, by considering the relation of the reduced silver to the nickel, the same result is arrived at.

Total nickel found	0·4251 grm.
Nickel equiv. of silver	0·2840 „
Difference	0·1411 „

Complying exactly with the equation—

$$M_3O+4AqNO_3=2Ni_2(NO_3)+NiO+4Aq.$$

There can therefore be no doubt that it is a hydrated suboxide of nickel with the formula $Ni_3O_2H_2O$. Such a compound was foreshadowed from the results of the preliminary experiments mentioned in the previous communication, although from the position of nickel in the periodic system Ni_2O might rather have been expected. This, however, cannot be reconciled with the results of the analysis of the oxide, prepared at different times and under different conditions. It is just possible also that this is the oxide which is formed when alkaline stannous chloride is allowed to act on hydroxide of nickel. On heating a mixture of the two substances, the green oxide takes a darker shade and finally becomes quite black; but inasmuch as the product is rendered highly impure with different tin compounds, I have not yet decided the matter.

Nouméa, New Caledonia,
November 30, 1894.

THE SOLUBILITY OF BASIC SLAG.

In a paper read before the Cleveland Institute of Engineers,* C. H. Ridsdale discusses certain statements published as Professor Wagner's, and current impressions relating to the "fertilising activity" of various makes of basic slag as measured by the citrate solubility of the phosphoric acid, some of which, particularly the third, were in his opinion misleading.

1. That this solubility represented or was closely parallel to the availability for plant life under actual agricultural conditions.
2. That the more soluble slags were also generally higher in silica.
3. That slags having a higher "percentage solubility" were more valuable than those with a low percentage solubility, though the former might contain only 10 per cent or 12 per cent total phosphoric acid, as against 17 per cent or 18 per cent in the latter.

An instance of the third proposition cited was in a pamphlet, which was a translation of a paper by Professor Wagner published presumably for farmers, in which were tables giving numerical values to slags of different makes, which as printed were altogether incorrect, a slag having 8·44 per cent soluble phosphoric acid being valued at 100, whilst one having 14·48 per cent, nearly twice as much, was only valued at 81, simply because only this percentage of the total phosphoric acid was soluble. These values held good per unit, but this had not been stated, and in consequence of such statements entirely false impressions had been created, which it was important to remove, as they might be most serious to makers and farmers.

He had carefully examined the six crystalline constituents of basic slag, three of them phosphoric, and three non-phosphoric, some of which Mr. Stead and himself had discovered and described for the first time to the Chemical Society and Iron and Steel Institute early in 1887.

He had also examined a number of basic slags, including three of the North Eastern Steel Company's make (which gave very good results), and a number of other British makes, all of a degree of fineness as put on the market, as well as siliceous cinders for comparison. Of these he had determined the "citrate solubility" by Professor Wagner's method, together with the effect of friction on the same, the composition and the carbonic acid water solubility, and had drawn up a number of tables and diagrams (which were shown by means of lantern slides kindly prepared by Mr. Stead) illustrating the results.

He showed that that portion of the phosphoric acid not soluble in the first treatment by the "citrate" test as conducted, is not necessarily unavailable for plant life, even during the first year, as extended conditions such as:

1. More solvent.
2. Greater degree of fineness.
3. Longer time.
4. Friction such as may take place between the earth and the slag, &c., may render it all soluble.

That pure tetrabasic phosphate of lime, whether natural (as in the transparent plates) or artificial (as prepared synthetical by Mr. Stead), are completely soluble, and as readily so as the blue crystalline variety, if the citrate used is proportioned to the phosphoric acid present.

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* January 14, 1895, with which is incorporated an appendix prepared afterwards.

That increased quantities of poorer slags, containing the same quantity of soluble phosphoric acid as richer varieties, and which should when treated with fixed quantities of solvent (as would under actual agricultural conditions be the case) yield an equal amount, do not, but yield much less.

He dissented strongly from the expression of results in terms of "percentage solubility," and drew many comparisons between this and the absolute solubility.

His earlier experiments showed the alleged close relation between the silica content and the "percentage solubility" to have almost as many exceptions to as examples of the rule, and that there was a point beyond which the higher the silica the less the solubility. He contended that only practical tests extending over years could show the real value of slags of different degrees of solubility, and that next to this would come carbonic acid water tests.

He therefore sought further for the principles governing this, and after determining what bodies the citrate solution dissolved preferentially, as well as from a close study of the behaviour of whole series of samples, and of other evidence adduced, felt there was good ground for the following conclusions.

The "*Percentage Solubility*" depends on:—

1. The actual content of phosphoric acid varying inversely to it.
2. The neutrality or freedom from excess lime (and possibly certain other bases).
3. That silica does not *per se* increase this, but only:—
   - *a.* When it combines with and thus neutralises excess of lime, and possibly certain other bases.
   - *b.* When as a condition of the presence of a large quantity of silicate of lime (which silicate appears not to interfere with the solubility in the quantities in which it is generally present) there is only a low total percentage of phosphoric acid present.
4. That silica decreases this when present in quantities greater than required in 3, or sufficiently large to bring about the formation of silicates of iron or manganese.
5. That excess of oxides of iron and manganese have a very small effect, almost negligible when compared with that of lime, the actual solubility being the resultant of the inert action of each of these conditions as are present.

The *Absolute Solubility*, or actual amount dissolved, depends on:—

1. The actual content of phosphoric acid, varying directly with it, and in other respects following 2, 3, 4, and 5.

From these conclusions he showed that if any maker's slag has a poor solubility it is necessary in the first place to determine to which of these causes this is due, in order to decide what cure to adopt, or whether any is practicable.

THE SECRET OF THE BROWNIAN MOVEMENTS.*

By R. MEADE BACHE.

(Continued from p. 48).

The account of the views of Herr Wiener in the *Jahresberichte* makes an important omission. It devotes itself chiefly to reciting what, in his view, does not cause the brownian movements, but does not mention precisely to what he does ascribe them. Herr Wiener says, in the last paragraph of his article, in *Poggendorf's Annalen*, 1863: "The weight of the preceding conclusion, that one cannot ascribe the trembling movement to any exterior cause, is very greatly added to by the ascertained fact that the diameter of the similarly moved water masses is so small that it nearly corresponds with the wave-length of red light, and still more closely with that of radiant heat." This passage gives the key-note to his views on the brownian movements. After a most elaborate series of experiments, in which he measured on a micrometrically divided glass slide, with the addition of diagonal lines, and by watch, the range and the time of the movements, he reached his most important conclusion, that, because the dimensions of the aforesaid wave-lengths of light and heat have a certain close correspondence with the diameters of the minutest particles and water masses, they form the moving impulse of the motions of the particles. He pictured to himself that the ether surrounding the particles, being continuous with the ether of space, acts, through the rays of light and heat on the particles and minute water masses, generating in their interaction, as the visible resultant of the forces in play, the movement of the particles in suspension in aqueous solutions. But if the cause of the movements assigned by Herr Wiener were the true one, the same cause ought to be operative in the case of alcohol and in that of the fixed and volatile oils; but it is not. This conclusion of Herr Wiener's seems to me to be derived from the unsatisfactory fact of a coincidence, of which kind of proof we habitually perceive more than enough to obscure, bewilder, and often to baffle our feeble efforts to penetrate beyond the veil of phenomena, of things as they seem, to the everlasting noumena, things as they are, near the inscrutable throne of nature.

I will not weary my hearers with the recital of the numerous details of my own experiments, the names of the substances that I tried, the modes in which they were treated, the manipulations of various sorts necessary to the prosecution of the work. Everyone knows the difficulties that will arise in new investigations, which will themselves suggest the means of countervailing them as the work proceeds. In this particular case one difficulty was to obtain finely enough divided matter in other liquids besides water. It may be interesting to mention that I did not read anything on the subject until my own experiments were nearly finished. By this course I avoided any possible bias expressed or implied in the directions to be pursued and the conclusions to be drawn, and I had ultimately the satisfaction to perceive, as I had often before observed, how, owing to the constitution of the mind, men necessarily follow the same general and often particular track in their procedures. It is not in the course they follow that they differ much, but in the conclusions which they reach in pursuing what is virtually the same way. Fortunately for me, constrained to be absent for months in the field on geodetic duty, and at all times constantly engaged at my profession, night still lent itself to my slowly accumulated results. That the investigation was most interesting, I need hardly say.

As electric currents have been demonstrated in the human body, I naturally thought that all slight differences of tension between the liquid and particles, or in the liquid itself, might set up electric currents. Therefore I passed the galvanic current through liquids filled with particles, watching them carefully. There was not the slightest visible effect thereby produced on the movements of the particles. If the movements had been produced by electric currents, then so strong a current as I often passed through a drop of water ought to have left no manifestation of movement possible from the necessarily weak, if actually existing, currents supposed to be actuating the particles. The molecular movement, so-called, is, as described by Herr Wiener, a zigzag one, but that term does not exactly convey the peculiarity of the motion. It is a combination of a jerky, wobbling movement, performed within determinate bounds, entirely irrespective of the sweep of currents in the liquid, or even

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* Read before the American Philosophical Society, April 20, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii, No. 145.

of the effects in some cases of terrestrial gravity, and in no case seemingly affected by the influence of local gravitation of particle to particle. Taking the vermilion of the sulphide of mercury, as finely divided as it can be made, and turning the microscope at even a slight angle from the vertical, the effect of terrestrial gravity on the particles becomes at once apparent, but taking the carmine, reputedly made of cochineal, the particles are not affected in the slightest degree by terrestrial gravity. Of course it is hardly necessary to say that any solution should be weak, in order to allow the substances under examination to receive the finest division of which each is susceptible as dissolved. The specific gravity of sulphide of mercury is not only much greater than that of cochineal, but additionally it is not susceptible of nearly so minute division as cochineal is. Of all substances that I experimented with, cochineal seemed to be that which is capable of the finest division, and at the same time of the most brilliant illumination. Gamboge, which appears to be the substance of predilection among many persons to experiment with for the brownian movements, offers nothing comparable to the brilliancy and the fineness of particles of carmine derived from cochineal. With a weak aqueous solution of carmine one may see by daylight, on a background of faint blue, and by ordinary artificial light, on a golden one, thousands of tiny particles, bright as sparks of ruby, shimmering and performing their independent evolutions over the field of view.

Just as one sees a boat managed by an unskilful helmsman pursue its erratic way in going about, being taken aback, or heeled over by a flaw of wind, without for a moment attributing its movement to currents or any other cause but the true one, so the constant observer of the brownian movements knows full well that the particles themselves are moving, not being moved by currents or by gravitation towards the earth or among themselves. He, from the first, recognises the fact that the smaller the particles are, the more vivid is their movement. He recognises another, that, although many large particles do not, as masses, move at all, yet the larger masses are all alive, as it were, with smaller ones, seen clearly around their periphery, on the silhouette of which they are seen plying like banks of oars in an ancient trireme. He is struck with and convinced of still another thing, that whereas one might expect to find that all particles would manifest an attraction for each other through gravitation, and that the larger and largest, but all in proportion to their relative size, would attract and absorb the relatively smaller and smallest ones, nothing of the kind occurs, but the smaller, down to the smallest, go their own way, sometimes even touching the largest and bounding off and away as if they do not, as indeed they do not visibly, submit to the force of gravitation. Of course they cannot escape the influence of gravitation, whether terrestrial or among themselves, but the effect of gravitation upon them is masked, in what manner will appear later.

It seemed to me that magnetic earth-waves might affect particles in such delicate suspension as those of which we are speaking, some of which are no greater in diameter than 1-100,000 of an inch, seen under various powers capable of magnifying from 650 to 1300 diameters. Accordingly, I have placed the particular fluid under examination in the lines of force of a permanent magnet, with the magnet on one side and the keeper on the other of the drop of fluid. Concentrating the gaze on individual particles, to observe if their movement were modified, and then on others in succession, and often repeating the experiment, nothing could be observed other than the movements existing before the magnet had been brought into requisition. The only kind of particles susceptible to the influence of the magnet were those of precipitated iron, but iron is always obedient to the magnet.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 8th, 1895.

Prof. A. W. Rücker, F.R.S., President, in the Chair.

The Treasurer, Dr. Atkinson, presented his report for the year 1894. The balance sheet showed a somewhat larger expenditure than in previous years; the increase being partly due to the new system of publishing abstracts, partly to the rent of rooms and the expenses of tea. The balance in the bank had increased by about £33 during the year, but the Treasurer said that, strictly speaking, the Society had trenched on its capital to the extent of about £30, and that this would probably be the last report for some time to come which would show a balance in favour of the Society. The assets of the Society exceeded its liabilities by £2642 0s. 5d.

Prof. Carey Foster asked whether it would not be possible, in estimating the assets of the Society, to make some allowance for the stock in hand.

Dr. Atkinson replied that that had not hitherto been done, and the difficulty would be to assign a money value to the stock. The stock of the works of Joule and of other memoirs was, of course, decreasing, while the sale of the *Proceedings* was becoming somewhat greater. As regarded the securities of the Society, their actual value would be about £200 or £300 more than appeared on the balance-sheet.

Prof. Rücker said that the Society had deliberately entered upon a policy of expansion, and that they must be prepared to find the expenditure increasing. On the other hand, it was hoped that, by making the Society more attractive, a greater number of persons would be induced to join. In view of the great advantages now enjoyed by members, there had been some suggestion of raising the subscription, but in any case he thought that they might look forward to the future with confidence. The report was then moved and adopted.

The next business was the election of Officers and Council for the year 1895-6, and Messrs. Rhodes and Yule, being asked to act as scrutators, collected the balloting lists.

Prof. Carey Foster proposed a vote of thanks to the Lords of the Committee of the Council on Education for having allowed the Society to meet at the Royal College of Science. At the commencement of the life of the Society, its founder and first president, Guthrie, had obtained permission for the meetings to take place at South Kensington, and the Society had continued to meet there until their recent migration to the rooms of the Chemical Society. The vote of thanks was duly seconded and was carried unanimously.

Major-General Festing then proposed, and Mr. Croft seconded, a vote of thanks to the auditors, Messrs. Inwards and Trotter. This also was carried.

Mr. Trotter then proposed a vote of thanks to the retiring Council. They had shown an energy which was rare in such societies, and had inaugurated an active and original policy which must prove of the greatest benefit to the Physical Society and to physical science generally. Carried unanimously.

Mr. Elder gave notice of a proposed alteration of the Rules, the object being to allow the Council, under certain conditions, to admit persons into the Society without requiring from them the usual number of recommendations from members. It was pointed out that sometimes eligible persons, especially those resident abroad, were unable to enter the Society because they were unknown to any of the existing members. The motion to sanction the proposed alteration was put from the chair and carried, but this decision will need to be confirmed at a subsequent meeting, of which due notice will be given.

Mr. Rhodes then read the following list of Officers and Council elected for the year 1895-6:—

President—Captain Abney.

Vice-Presidents who have filled the office of President—Dr. Gladstone, Profs. Carey Foster and Adams, Lord Kelvin, Profs. Clifton, Reinold, Ayrton, Fitzgerald, Rücker.

Vice-Presidents—Mr. W. Baily, Maj.-Gen. Festing, Prof. Perry, Dr. Stoney.

Secretaries—Messrs. Blakesley and Elder.

Treasurer—Dr. Atkinson.

Demonstrator—Prof. Boys.

Other Members of Council—Mr. Shelford Bidwell, Prof. Crookes, Messrs. Fletcher, Glazebrook, G. Griffith, Profs. Henrici, Minchin, Mr. Swinburne, Profs. S. P. Thompson and S. Young.

Prof. Rücker then vacated the chair in favour of Captain Abney, and the meeting being then resolved into an ordinary meeting,

Mr. W. B. Croft gave "*An Exhitition of Simple Apparatus.*"

An optical bench was shown which consisted of a wooden lath of rectangular section, furnished with a millimetre scale, and clamped on to the table, together with three flat wooden blocks, whose contacts with the table and the lath left them only freedom to slide in a direction parallel to the scale.

Another apparatus was designed for observing anomalous dispersion. A cork supported two rectangular pieces of microscope cover-glass, which were inclined at a small angle to one another; and a drop or two of a strong alcoholic solution of fuchsine being introduced between them was maintained in position by capillary action. Photographs were shown of Chladni's sand-figures, some of the forms being of an unusual character.

Mr. Croft also exhibited a polariscope in which the polariser was a thin piece of glass stuck into cork by means of black sealing-wax, and the analyser a plate of tourmaline; as well as a miniature model of Grove's gas battery.

Photographs of some curious optical phenomena were projected on the screen, including 12-rayed stars, seen on looking at a bright source of light through certain specimens of mica, and pairs of intersecting or non-intersecting circles of light obtained under similar circumstances with (doubly-refracting) fibrous calcite. These last, it was suggested, were similar in origin to the curves obtained by reflection at, or transition through, a diffraction-grating held obliquely.

Clock-springs broken by frost were also exhibited, each spring having given way in a very great number of places simultaneously.

Dr. Johnstone Stoney said that many years ago he had published in the *Transactions of the Royal Irish Academy* an investigation of the circles seen in fibrous calcite, and had shown geometrically that they had nothing to do with the regularity of the fibrous structure, but were due to reflection and refraction within the crystalline plate. The distribution of the planes of polarisation round the circumferences of the circles was also accounted for by his investigations.

Mr. Price said he had found that when a clock-spring during the process of hardening was kept in shape by wires, subsequent fracture was most apt to occur at those places where the wires had been in contact with the spring.

Mr. Rhodes asked if Mr. Croft had ever tried Newton's experiment of admitting sunlight between two sharp edges inclined at a small angle to one another. He had not been able to obtain the hyperbolic bands described by Newton.

Mr. Croft said he had not tried the experiment exactly in that form.

Capt. Abney said that the experiment had succeeded very well in his hands.

Mr. S. Skinner read a paper "*On the Tin Chromic Chloride Cell.*"

He said that his attention had been attracted to the cell by an account published by Mr. Case, of New York. The cell had been stated to give no E.M.F at ordinary room temperatures, while it gave a considerable E.M.F. at 100° C.

The author had found that when the cell was directly connected up to a galvanometer, there was no current at ordinary temperatures, and some current at 100° C., but when he had measured the E.M.F. by Poggendorff's method he had found 0·44 volt at 15° C., and 0·40 volt at 97° C. The cell, as originally described, consists of a tin plate and a platinum plate immersed side by side in a solution of chromic chloride; when the temperature of the cell is near to 100° C. and the poles are connected, the following reaction occurs:—

$$Cr_2Cl_6+Sn=2CrCl_2+SnCl_2;$$

and when the poles are disconnected and the cell cooled, the reverse change takes place. The author prefers to use as electropositive metal an amalgam of tin and mercury instead of a tin plate, so that when the tin precipitated during cooling falls to the bottom of the solution, it is re-dissolved in the mercury, and the cell has regained its original state. When silver nitrate solution is added to chromic chloride, only two-thirds of the chlorine comes down as silver chloride, and this has led the author to suppose that the proper formula for chromic chloride is $2CrCl.Cl_2$. Hence he works out the electrolytic action by means of a Grotthus chain.

Prof. Rücker asked whether a change of polarisation would explain the behaviour of the cell at different temperatures.

Prof. Carey Foster asked whether the reversed chemical action on cooling from a high temperature were accompanied by a reversed E.M.F.

Mr. Skinner said no; the tin was precipitated throughout the solution, and not at the surface of the tin plate, so that no E.M.F. of the kind was to be expected.

Mr. Appleyard thought that Prof. Minchin had used tin chloride cells with two tin plates for electrodes, the cells only working when one plate was illuminated.

Mr. Trotter wished to know whether heating the cell supplied energy to it, or simply removed an obstacle in the form of polarisation.

Mr. Skinner thought that heating acted by removing an obstacle.

Capt. Abney—And so doing work.

NOTICES OF BOOKS.

What is Heat ? A Peep into Nature's most Hidden Secrets. By Frederick Hovenden, F.L.S., F.G.S., F.R.M.S. London: W. B. Whittingham and Co., Limited. 1894. 8vo., pp. 350.

This is a very remarkable book and the outcome of a remarkable work. The author is a busy man of the busy world, who spends his leisure in the investigation of natural phenomena, not by the more laborious methods of what we may call "official science," but on an original and independent plan, characterised by a boldness amounting almost to audacity, and quite refreshing as a subject of contemplation and a relief from the uncompromising severity of mathematico physical treatises. We who spend our days in laboratories in the hum-drum work of worrying out particular issues and proximate truths can hardly refuse a full measure of admiration of a thinker who quietly brushes aside the monumental structures which we owe to the genius and patient elaboration of such philosophers as Joule, Clausius, and Maxwell, and pokes fun at a generation of physicists who have been proud to fall into line under their leadership. To put it briefly, the author deliberately poses as a rebel. We know from history that the only justification of rebellion is success; the dire alternative is usually the loss of a head.

This issue the author does not hesitate to challenge. It is true that he exhibits an occasional distrust of his ability to carry the position, and is inclined to plead with his friend the enemy. But the pleading is perhaps rather with "the layman," by whom, to use the author's words, "the verdict will in the main be given, and to whom the issues are of the greatest importance."

The author is anxious that the book shall make its mark, not merely on its self-contained merits, but because he feels a further call to attack the problems "what is electricity"? "what is life"? for the solution of which he is of opinion "that science has sufficiently advanced." This appeal perhaps is hardly ingenuous: it adds to the responsibility of the critic by introducing contingent and somewhat irrelevant issues. We confess that our judgment of the work would not be uninfluenced by this promise of contributions to even more burning subjects than the theory of heat, subject to favourable consideration of "these presents." Whether the author will feel encouraged by our appreciation of his work to address himself to this magnificent crescendo of effort we have no opinion. We deliberately close our eyes to the vista of scientific speculations opened up by the too suggestive preface, and shall be content to arrive at a fair judgment of the matter of the book as it stands.

The first section of the book is a criticism of "mathematical and physical concepts." The aim of the discussion is to disestablish the mathematician from what we should have considered his unquestionable position of leadership in the affairs of science. Mr. Hovenden twits him with the unreality of the most ordinary of mathematical operations. Thus "let us multiply −100 (*i.e.*, minus 100 objects or units) by −100 operations. The latter expression is unthinkable. But the mathematician says the result of the process, the product, is (plus) +10,000 objects!" This is then worked by the author to an apparent *reductio ad absurdum* as follows:—

We take two bowls, *a* and *b*. In *a* are 100 objects. We take the 100 objects out of *a* and put them in *b*. This is expressed mathematically $a-100$, $b+100$. Now multiply the contents of bowl *a* (−100) by −100 times, and then, says the mathematician, there are 10,000 objects in that bowl! "Can the operation be performed"? says the author. "Mr. Mathematician" is directed to take two bowls and 100 marbles and perform "the operation"; "then" (by inference) "we can believe in your fundamental ideas."

We don't know whether any mathematicians will read this book, and if so whether they will resent this and other efforts to materialise and ridicule their symbols and operations.

It appears to be a necessary part of the author's scheme to clear away the mathematical methods of handling quantities with which his own are irreconcilable. That is his own confession, implied in every section of the book. The author enters on the issue with a light heart and light language. He evidently has not studied De Morgan's "Budget of Paradoxes." There are many warnings in this classic of which he might have availed himself for the strengthening of his indictment. He will be the first to admit that it might have been stronger, and most mathematicians will agree. They will also be quite ready to stand aside in favour of Mr. Hovenden should he be able to climb the inaccessible peaks of "ethereal" truths by the direct method of "sensible" observation. And they will note that he claims to have done this.

Section II. is devoted to destructive criticism of the kinetic theory. We commend this section, as indeed the preceding, for a collection of well-chosen excerpts from the writings of Clerk Maxwell and others who have contributed to the elaboration of this remarkable theory. These excerpts constitute a fair general statement of the theory in question, to which the author advances certain particular objections. Instancing a silver coin of date B.C. 200, we are confronted by the author with the paradoxical hypothesis that the ultimate atoms of this extremely concrete object are, and have been, according to the "Kineticians," in a condition of intense heterogeneous motion. The second is based on the comparison of the condition of water with that of the gases of which it is composed, or into which it may be decomposed, respecting which we read in the book, "the temperature of the gas is exactly the same as was the water as measured by the thermometer, proving there is no more motion in the gas than there is in the water; so the dynamical theory cannot be true. The third "negation" of the theory is that supplied by the effect of releasing gases from pressure, and allowing them to impinge on the face of a thermopile, causing the reaction of "cold," together with the converse experiment of blowing upon the instrument with bellows, causing the opposite effect.

We do not propose to traverse the author's arguments. He is evidently, from the later section of the work, so entirely convinced by his "sensible" observations of being in possession of facts (and the key to them), which categorically upset every cardinal position of the modern physicist, that argument looks a little like trifling.

The succeeding section on "Gravitation and Weight" is similarly devoted to correcting "the confusions with which the specialists have surrounded themselves." Clerk Maxwell and Lord Rayleigh are especially singled out for treatment on account of their pronouncement that gravitation is not a force.

The section concludes with a statement of "the only concepts which can explain the facts." The position not being arguable, therefore—with the author—the critic's task resolves itself into that of committing these further innovations to those who find rest in lucid finalities rather than in the complex equilibrium of proximate gropings.

The last sections of the book are the most original by far. They contain a careful description of a number of very interesting experiments and observations, preceded by a "statement of the case" or, *à priori*, formulation of the author's view of the micro-cosmos. This view is nothing less than remarkable. There are very few scientific men who are prepared with anything like a complete *credo* in regard to the constitution of matter, or the still more "elusive" quantity known as "ether." Mr. Hovenden has given us an object-lesson of boldness in reducing the results—evidently of years of thought—to a comprehensive statement in twenty-three "articles." The author's most important conclusions are that "the ether" is an "anti-gravitating fluid"; that the atoms and molecules—the ultimate forms of matter—are of variable form and dimensions; the difference in dimensions is due to variations "of the quantity of ether held by them at a given moment, and is what is called the *temperature* of the atom or molecule"; and lastly that both *ether* and *molecules* may be brought to visual demonstration, may be *seen* under conditions which it has been a main endeavour of the author to devise.

As we said, these extraordinary views are formulated as a "statement of the case," preceding the experimental and demonstrative section of the book. In these experiments the author shows a good deal of ingenuity. Every student accustomed to the strictly quantitative methods of modern science would find himself very much puzzled by the paradoxical observations which Mr. Hovenden is able to create and put before him in such form as to be undeniable. His intuitive scepticism would at once suggest the question: Can these observations involving not a single quantitative measurement constitute a destructive criticism of a science which only began to move with the entrance of the quantitative method, and has progressed *pari passu* with the reduction of the phenomena to mathematical expression? His most natural criticism would be "there must be something wrong somewhere," and he would proceed to vary the conditions of the demonstrations in every possible way with the view of locating that something.

However, it is quite impossible in the compass of this brief notice to follow our supposed student of the modern order in a detailed criticism of the phenomena designed to upset his cherished "apple cart." As we said at the beginning, the author is a rebel, and justifies his rebellion so far that he commits himself to a plain and categorical description of phenomena which he finds irreconcilable with the current theories of thermodynamics.

Heterodoxy is always interesting—sometimes from the matter of the dissent, more often from the form. It plays an important part in history, though we are bound to say a diminishing part in the history of the natural sciences.

The book we have thus briefly noticed is an extraordinary manifestation of the spirit of heterodoxy in a domain where it often receives short shrift. Mr. Hovenden knows his responsibility in this matter. We commend his work as an extremely interesting study to the metaphysician, and as affording ample entertainment to physicists not too exclusively dominated by the formal and academical view of their science or sciences.

OBITUARY.

Dr. GERHARD KRÜSS.

We have just learned, with profound regret, that Dr. Gerhard Krüss, Extraordinary Professor of Chemistry in the University of Münich, died on February 3rd at the early age of thirty-five years. Dr. Krüss was universally known and admired as founder and editor of the *Zeitschrift für Anorganische Chemie.* He was a worker from whom the philosophy of chemistry had much to hope.

CORRESPONDENCE.

ARGON.

To the Editor of the Chemical News.

Sir,—When lecturing on the atmosphere to my elementary class, it was necessary to discuss the new gaseous constituent announced by Lord Rayleigh and Professor Ramsay at the last meeting of the British Association, and I ventured to propound the theory that the new substance is an allotrope of nitrogen. The density of the gas discovered was given as 19·09, but it was admitted that some ordinary nitrogen still remained. If this last quantity of N_2 be removed, I anticipate the density would be 21; and the molecule of the allotrope be N_3.—I am, &c.,

Jas. Braik Mason, F.C.S.

Laboratory, Y.M.C.A., Constitution Road,
Dundee, February 6, 1895.

BORON CARBON BATTERY.

To the Editor of the Chemical News.

Sir,—In reply to Mr. C. J. Reed's remarks (Chemical News, vol. lxxi., p. 63), permit me to ask the writer where he obtains the information from as regards the existence of a platinum element in the battery described by me, while at the same time the title of the battery is distinctly stated "the boron carbon battery." Again, he uses the peculiar expression, as regards voltage, in "something over two of his three volts." Is this a Yankee bull, or does Mr. Reed expect one cell to dry up Niagara?—I am, &c.,

H. N. Warren.

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

THE PERIODIC LAW.

To the Editor of the Chemical News.

Sir,—In your last issue you print a short paper by Dr. Johnstone Stoney, in which he refers to the Periodic Law. In it, after referring to the probability that the free hydrogen has passed into space, he remarks: "The six other elements between hydrogen and lithium seem not to have been able to enter into, or remain in, combination under the conditions that prevailed at some stage of the earth's past history, and so these escaped—unless, possibly, a compound of some of them may yet be found." For convenience, he names these elements infra-beryllium, &c.

Now, I would ask, have we any right to say that Mendeleeff predicts any such elements, or that his table is intended to indicate that they exist? The table is printed at the beginning of vol. i. of "The Principles of Chemistry" (English Translation). Here four of the six blanks are filled in with hydrogen compounds. I would also point out that there is nothing in this table to show that Mendeleeff believes that other elements will be found to come between F and Na. Table III. in the second volume of the above-named work clearly shows this. Here we have the elements arranged in the order of their atomic weights. In note [6] we read:—"In this column the sign 〰〰〰〰 placed between some of the symbols indicates that these are unknown intermediate elements according to the periodic system, and the figure indicates the number of such unknown elements. Thus, between Di and Yb there are fourteen elements wanting. It is probable that certain of the rare elements which have been discovered, but are as yet insufficiently investigated, enter into these interspaces." The first sign of the kind appears in the table between Mo and Ru; the series up to this point being regarded as complete, for no missing elements are indicated either between H and Li, or between F and Na. As Douglas Carnegie, in his very excellent article on the Periodic Law ("Watts' Dict. of Chemistry") remarks:—"Mendeleeff expressly omits Series 2 in making some of his generalisations." The elements from Li to Mg are regarded as "typical elements." Their classification is admittedly unsatisfactory, and it would be unwise to draw sweeping conclusions from the table alone.—I am, &c.,

R. M. Deeley.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 4, January 28, 1895.

Raoul Pictet addressed to the Academy a new memoir entitled "Study of the Constitution of liquids and their Vapours at Temperatures near the Critical Point by Solutions of Solids in these Vapours."

A. Duponchel addressed two new memoirs concerning the "Adaptation of the Principles of the New Cosmogonic Theory to the Interpretation of the Formulæ of Chemical Combinations."

Stan. Millet addressed a "Project of Communication with the Planet Mars."

These memoirs were all referred to Commissions.

The Perpetual Secretary announced to the Academy the loss it had sustained in Dr. Gaston de Saporta, who died at Aix, on January 26, 1895.

Preparation and Properties of Iron Boride.—Henri Moissan.—The author has proved that at the temperature of the arc carbon unites with the metals, producing crystalline carbides, perfectly definite, such as aluminium-carbide, and the alkaline-earthy acetylides. Boron and silicon form in like manner series of definite crystalline compounds. The study of these new series will enrich chemistry with bodies, often very stable, some of which will doubtless admit of industrial applications, and will probably supply useful indications for determining the valence and the classification of the elements. Iron boride may be obtained by the action of boron chloride upon reduced iron, or by causing boron to act directly upon iron. Iron boride occurs in brilliant crystals of several m.m. in size, of a grey colour slightly yellowish. Its sp. gr. at 8° is 7·15. The crystals are stable in dry air or oxygen, but in presence of moist air they are covered with an ochreous layer. If heated in a current of chlorine at redness they are attacked with incandescence, and the chlorine unites with the boron. Bromine attacks this compound more readily, forming a double boron and iron boride. Iodine has no action at 1100°. It is the same with hydriodic acid. Oxygen attacks amorphous iron chloride more easily than the crystalline form. Amorphous boron is attacked by sulphur at a temperature little above its melting point. Potassium chlorate and nitrate do not attack iron boride at their melting-points, but if the temperature is raised, a reaction sets in and continues with incandescence. Melted alkaline carbonates rapidly destroy iron boride. The true solvents of iron boride are nitric acid and aqua regia. The theoretical composition of iron boride is—iron, 83·58; boron, 16·42. The figures actually obtained on analysis being—iron, 84·15; boron, 15·18, leading to the formula BoFe. On raising the temperature of the electric furnace at the moment of forming iron boride no other combinations have been obtained. At these high temperatures chemistry seems simplified, and we never obtain more than one compound of a very simple formula.

Action of an Electric Current on a Series of Metallic Sulphides in Fusion.—Jules Garnier.—The author concludes from his experiments that:—Sulphur combined with metals in a molten state in the absence of air, and traversed by an electric current, the electrodes (or at least the anode) being of carbon, there is doubtless a formation of carbon sulphide. In a mixture of molten metallic sulphides, excluded from air, and traversed by an electric current, the electric conductivity of the mixture remains *homogeneous* at each instant considered, increasing by degrees, in consequence of the successive elimination of the sulphur. As for the metals and the residual sulphur, they group themselves so that each elementary section of the bath, taken perpendicularly to the direction of the current, has the same electric conductivity. Setting out from such experiments it may be possible to explain certain phenomena observed, *e.g.*, the manner of the distribution of metals, sulphurised or not, found in veins.

Some Properties of Bismuth Sulphide.—A. Ditte.—Space permitting, this paper will be inserted in full.

Influence of the Ambient Medium on the Transformation of Amorphous Zinc Sulphide.—A. Villiers.—The author studies the influence of dilution, of the alkalinity of the liquid, of the presence of foreign salts, and of washing.

Carbonyl Bromide and Chloro-Bromide.— A. Besson.—Not adapted for useful abstraction.

Mixed Ether, or the Ammonium Derivatives of Hexamethyltriamido-triphenylmethane.—A. Rosenstiehl.—The author expresses by the collective symbol A the group $[(CH_3)_2N.C_6H_4]$, which does not admit of any modification in the metamorphoses. Hence, $A_3{\equiv}C{-}H$ represents hexamethyl - triamido - triphenylmethane, $A_3{\equiv}C{-}OH$ the carbinol, and $A_3{\equiv}C{-}Cl$ the corresponding chlorhydrine. This last substance is known in trade as crystalline violet. The alcohol, which acts as a solvent if we cause caustic soda to act upon $A_3{\equiv}C{-}Cl$, enters by its substance into the mol. to form bodies of the general form $A_3{\equiv}C{-}OR$, which are derivatives of the methane-oxymethane $CH_3{-}O{-}CH_3$. Their existence and their manner of formation brings into fresh prominence the alcoholic function which is one of the peculiarities of the rosanilines.

Acetic Ethers of the Sugars.—C. Tanret.—By the reaction of acetic anhydride upon glucose in presence of sodium acetate or zinc chloride the author obtains three crystalline pentacetic ethers, which he names α, β, and γ pentacetines.

Hexamethylamine.—M. Delépine.—The author has studied the molecular weight of hexamethylamine, its behaviour with mineral acids, the nature of its basic function, the formation of its substitution derivatives, the nitroses and their destruction by acids, and its hydrogenation.

The Coula Seeds from Congo.—H. Lecompte and A. Hébert.—The oily matter of these seeds, known as koumounou oil, is a trideine almost pure. It is a curious instance of a fatty matter containing only a single fatty acid.

Novel Practical Procedure for the Determination of Calcareous Matter in Arable Soils.—Antoine de Saporta.—This paper will be inserted in full.

Journal fur Praktische Chemie.

New Series, Vol. l., Nos. 11 and 12.

Complex Metallic Bases. Treatise I. Metallic Compounds of Thiocarbamide.—N. Kurnakow.—This elaborate paper does not admit of useful abstraction.

Communications from the Chemical Institute of the University of Kiel.—These communications comprise a first treatise by Th. Curtius on the derivatives of diamide with a closed atomic arrangement, and a second treatise by F. Wirzing on pyrazolin and some of its derivatives. Both these papers have already been inserted.

The Oil of the Root of Mignonette.—J. Bertram and H. Walbaum.—This paper is a communication from the laboratory of Schimmel and Co., of Leipzig. The root of the plant (*Reseda odorata*) contains a substance smelling of horse-radish. The oil is of a light brown colour; it has at 15° the specific gravity 1·067; it was slightly dextro-rotatory +1° 30′ in a column of the length of 100 m.m. At the ordinary atmospheric pressure the oil began to boil at 255°, but with decomposition. Even under reduced pressure it does not distil without decomposition. If boiled with sodium hydrosulphocyanic acid was found in the residue, proving the presence of sulphur in nitrogen. Hence the oil belongs to the class of the mustard oils. From its almost quantitative conversion into phenylethylamine, it must chiefly consist of phenylethyl mustard-oil.

Two New Laboratory Appliances.—H. Lœssmer.—The pieces of apparatus here described and figured are an agitator and a water-bath.

Reduction of Aromatic Nitro-Compounds.—H. Lœssmer.—Orthonitro substances have the property of not being attacked by alkaline arsenites. If ordinary commercial orthonitrotoluol is heated with aqueous solutions of this salt it is coloured dark yellow. The oil, which after reduction contains chiefly paratoluidin, with small quantities of azoxy-compounds as an impurity, is several times shaken up with hydrochloric acid and finally distilled over with watery vapours.

The So-called Stereo-chemistry of Nitrogen and J. H. van 't Hoff.—Ad. Claus.—A controversial paper.

MEETINGS FOR THE WEEK.

Monday, 18th.—Society of Arts, 4. (Cantor Lectures). "Means for Verifying Ancient Embroideries and Laces," by Alan S. Cole.
— Medical, 8.30.
Tuesday, 19th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "Paraguay," by A. F. Baillie.
Wednesday, 20th.—Society of Arts, 8. "Rule of the Road at Sea," by Admiral P. H. Colomb.
— Meteorological, 8.
— Geological, 8.
— Microscopical, 8.
Thursday, 21st.—Royal, 4 30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Meteorites," by L. Fletcher, M.A., F.R.S.
— Chemical, 8. Ballot for the Election of Fellows, "The Electromotive Force of an Iodine Cell," by A. P. Laurie. "Contributions to the Chemistry of Cellulose," by Messrs. Cross, Bevan, and Beadle. "The Melting-points of Mixtures," by H. Crompton and Miss M. A. Whiteley. "The Volumetric Determination of Manganese," by Messrs. J. Reddrop and H. Ramage.
Friday, 22nd.—Royal Institution, 9. "Atmospheric Electricity," by Prof. A. Schuster, F.R.S.
— Physical, 5.
Saturday, 23rd.—Royal Institution, 3. "Moore's Irish Melodies" (with musical illustrations), by Sir Alexander Campbell Mackenzie, Mus. Doc.

Alembic Club Reprints of Historical Works relating to Chemistry.

RESEARCHES on THE ARSENIATES, PHOSPHATES, and Modifications of Phosphoric Acid. By Thomas Graham, F.R.S. (1833). *Just published*, crown 8vo., cloth, 1s. 8d. post free.

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Sealed Tenders, endorsed "Tender for Acid," addressed to the Chairman of the Gas Committee, to be delivered to my Office, Town Hall, Salford, not later than 3 p.m. on Thursday, February 21st.

(By Order) SAML. BROWN, Town Clerk.
Town Hall, Salford,
February 8, 1895.

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GAS DEPARTMENT.

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Sealed Tenders, endorsed "Tender for Tar," addressed to the Chairman of the Gas Committee, must be delivered to me not later than 3 p.m. on Thursday, the 21st instant.

(By Order) SAML. BROWN, Town Clerk.
Town Hall, Salford,
February 8, 1895.

A GUIDE TO STEREOCHEMISTRY, with an INDEX TO THE LITERATURE. By Arnold Eiloart, Ph.D., B.Sc. (Lond.). Illustrated with Fifty Woodcuts and Five Plates. 8vo. 4s. post free. [1893.

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THE CHEMICAL NEWS.

Vol. LXXI., No. 1839.

ON THE RATIO OF THE SPECIFIC HEATS OF SOME COMPOUND GASES.*

By J. W. CAPSTICK, D.Sc., M.A.,
Fellow of Trinity College, Cambridge.

The experiments described are a continuation of those of which an account was given in the *Philosophical Transactions*, vol. clxxxv., p. 1.

The apparatus and method of procedure were the same as were described in the former paper. Kundt's dust-figure method was used for finding the velocity of sound in the gas, and the ratio of the specific heats was calculated by means of the formula—

$$\gamma=1\cdot408\times\rho\times\left(\frac{l}{l'}\right)\left\{1+\frac{1}{p}\frac{d}{dv}(pv)\right\},$$

the last factor being added to the ordinary formula in order to correct for the deviation of the gas from Boyle's law.

The densities and isothermal curves were determined experimentally.

The results are as follows:—

Name.	Formula.	γ.
Methylene chloride	CH_2Cl_2	1·219
Chloroform	$CHCl_3$	1·154
Carbon tetrachloride	CCl_4	1·130
Ethylene chloride	$C_2H_4Cl_2$	1·137
Ethylidene chloride	$C_2H_4Cl_2$	1·134
Ethylene	C_2H_4	1·264
Vinyl bromide	C_2H_3Br	1·198
Allyl chloride	C_3H_5Cl	1·137
Allyl bromide	C_3H_5Br	1·145
Ethyl formate	$HCOOC_2H_5$	1·124
Methyl acetate	CH_3COOCH_3	1·137
Sulphuretted hydrogen	SH_2	1·340
Carbon dioxide	CO_2	1·308
Carbon disulphide	CS_2	1·239
Silicon tetrachloride	CCl_4	1·129

From these and the results given in the former paper it is shown that corresponding halogen derivatives of the same hydrocarbon have the same γ, the statement being no longer restricted to the monohalogen derivatives of the paraffins.

The equality of the γ's of the two dichlorethanes, and of methyl acetate and ethyl formate, shows that the previously investigated case of the two propyl chlorides does not stand alone, but that it is probably true that isomeric bodies in general have the same γ.

From the results of the substitution-products of methane and ethane with more than one halogen in the molecule it is shown that, whether the first chlorine introduced into the molecule alters the value of γ or not, each chlorine after the first causes a fall in γ.

$SiCl_4$ has the same γ as CCl_4. SH_2 has nearly the same γ as some observers have found for OH_2, but CO_2 and CS_2 differ widely, whence it follows that, just as in the case of hydrogen and chlorine, the possibility of interchange of oxygen and sulphur without altering γ does not extend to the substitution of two atoms of sulphur for two of oxygen.

In the paper a proof is given of the formula—

$$\beta+1=\frac{\frac{2}{3}+\frac{1}{p}\frac{d}{dv}(pv)}{\gamma-1}$$

for calculating θ, the ratio of the rates of increase of intramolecular energy and translational energy of the molecule on a rise of temperature, and the constant β is given for the gases investigated.

It is shown that—

$$\frac{\beta+1}{n}$$

is constant for the paraffins and their monohalogen derivatives, whence it follows that for these the ratio of the increase of mean total energy to the increase of kinetic energy of translation of the molecule is proportional to the number of atoms in the molecule.

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[*] Abstract of a Paper read before the Royal Society.

ON THE

NATURE OF THE SUPPOSED NEW ELEMENT PRESENT IN THE ATMOSPHERE.

By T. L. PHIPSON, Ph.D., F.C.S., &c.,
Formerly of the University of Brussels, and the Laboratoire de Chimie Pratique, Paris.

In the series of papers published by me in the Chemical News during the last two years I have brought forward many facts and arguments to show that the primitive atmosphere of the earth consisted of nitrogen alone, and that the whole of the oxygen now present in the air is due to plant life.

In these researches it was found that all plants are by nature essentially anaërobic.

It was also pointed out that nitrogen is the only element that could have formed our primitive atmosphere, on account of its extremely neutral or inert character.

After having paid so much attention to the nature of atmospheric air, I was much interested in perusing in a recent number of the Chemical News (vol. lxxi., p. 51) the account of the laborious and ingenious experiments of Lord Rayleigh and Prof. Ramsay on the existence of a supposed new element in the air, to the extent of about 1 per cent, which had hitherto been overlooked.

The reading of their paper has convinced me that the substance is an allotropic form of nitrogen, and that the day will come when they will succeed in converting it into cyanogen, ammonia, and nitric acid. As they show, it was already in the hands of Cavendish in the last century, as a residue of the sparking of nitrogen and oxygen.

When bodies are changed to an allotropic condition in this way their characteristic properties are enhanced. So for oxygen its activity is greatly increased, but for nitrogen the inert character would become more apparent.

According to Lord Rayleigh's figures, the substance called "argon" would be 3 molecules of nitrogen condensed into two molecules, somewhat analogous to what Andrews found for ozone as compared to ordinary oxygen.

The Casa Mia Laboratory, Putney,
London, S.W., Feb. 9, 1895.

LORANDITE, A NEW THALLIUM MINERAL.

A new thallium mineral has just been described, under the name of Lorandite, by Professor Krenner, of Buda-Pest. The new mineral occurs sparingly, in association with realgar, at Allchar, in Macedonia. It is found as transparent crystals belonging to the Monosymmetric system, and having the form of plates or short prisms. Its colour varies from cochineal-red to kermesite-red. The mineral proves on chemical analysis to correspond to the formula $TlAsS_2$.

	Observed.	Calculated.
S	19·02	18·67
As	—	21·87
Tl	59·51	59·46

AN ATMOSPHERIC PURIFIER.

By JOHN B. COPPOCK, F.C.S.,
Science Master, Camberwell Institute.

When a flocculent solid body falls through a fluid it drags down in its falling suspended matters contained in the fluid.

We should therefore expect that snow falling through the atmosphere will cleanse it by taking out most of the suspended matters. The present year has afforded many opportunities of getting a quantitative value for the purifying action of snow.

The first analysis gives figures yielded by snow collected in the suburbs of London, where the district is fairly open. This snow fell on January 13th, having a depth of 4 inches approximately. One characteristic of this snow was its great porosity, the crystals were also regular; both indicating that the snow was formed in a calm atmosphere.

The snow was melted and then analysed as water, the impurities being stated in grains per gallon.

Total solid matter	10·65
Mineral matter	5·75
Carbonaceous matter.. ..	4·90
Free ammonia	3·20
Albumenoid ammonia . ..	4·62
Oxygen to oxidise	0·721

A further analysis was made of snow from the same district after the fall of January 30th. The result was almost identical with the above figures; but this fact came out, that the first few strata of snow contained the largest amount of impurities. Fifty per cent of the snow's thickness yielded 75 per cent of the impurities.

An analysis of the snow of January 30th was also made upon snow collected in the quadrangle of Somerset House. The following shows the difference in the impurities. The physical condition of this fall was favourable to its picking up in its meshes much suspended matter.

Total solid matter	17·32
Mineral matter	6·25
Carbonaceous matter.. ..	11·07
Free ammonia	4·65
Albumenoid ammonia . ..	6·50
Oxygen to oxidise	1·16

The carbonaceous matter in each sample was ordinary soot particles.

These figures point out the value of a fall of snow from a manurial point of view, and also its value from a hygienic point of view. In a city where the air is often saturated with carbon particles, a fall of snow may he regarded as a mechanical contrivance of no mean value.

A NEW METHOD FOR THE ANALYSIS OF ZINC AND COPPER ALLOYS.

By H. N. WARREN, Research Analyst.

The following method of separation of zinc from copper and other allied metals, which was introduced by the author at the commencement of the present year, and is now being satisfactorily worked in several commercial laboratories, depends chiefly upon the superior affinity of magnesium to replace not only copper and metals of the same group, but by suitable means to effect a complete separation of such oxidisable metals as zinc, iron, &c. The method, although speedy and accurate, is perhaps better suited in cases where an approximate idea is known as to the nature of the alloy qualitatively. In the case of the sample presented being a brass alloy, which should, for convenience sake, be obtained in the form of filings, a suitable weighed quantity is introduced into a small conical flask, to which is added strong H_2SO_4 in proportion to the quantity of sample taken. On applying a gentle heat from a sand-bath for a few minutes, the alloy is quickly rendered soluble, and the whole diluted with water to a convenient bulk.

A few coils of magnesium tape are now introduced into the solution, and the solution maintained at about 100° F., until the whole of the copper is precipitated, which is ascertained by the absence of a red precipitate upon the addition of a drop of potassium sulphocyanide to the filtrate. The precipitated copper, which should be of a perfect red colour, is filtered, and finally washed into a tared platinum dish by the aid of a small quantity of ether, and dried in the air-bath, from whence the weight is readily obtained by the usual method. If tin, antimony, or other metals of the same group are suspected, the copper must necessarily be further examined. To the filtrate is added a somewhat strong solution of sodium acetate, and the whole raised to the boiling-point. By this means any free sulphuric acid is neutralised, all the iron that may be present is precipitated as tribasic acetate, and the sulphate of zinc present converted into acetate.

Into this is introduced a further quantity of magnesium, and in this instance the form of thick sheet or rod is better adapted than that of tape, the precipitated zinc being the more readily detached from the same. Upon the introduction of the magnesium, a brisk reaction follows, accompanied by a copious supply of hydrogen, the zinc being entirely precipitated, insomuch that not the slightest precipitate is obtained on the addition of ammonia and ammonium sulphide to the filtrate, the zinc thus obtained being treated as in the former instance, which, if successfully performed, shows very slight signs of oxidising.

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

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending January 31st, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, February 11th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 161 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 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 all respects the chemical composition of the five Thames-derived waters in January is a little better than that of the corresponding samples for December. The effects of the floods have passed away, and although the severe frosts have checked aquatic vegetation and thus tended to diminish the oxidation of organic matter through the influence of plant life, this diminution is not perceptible, the organic matter being a trifle less than it was last month.

In spite of the difficulties of filtration when the surface of the filter beds are liable to be frozen, only three samples were recorded as "clear but dull," the whole of the other samples being clear, bright, and well filtered.

The rainfall over the Thames valley has been slightly in excess of the twenty-five years average, which is 2·26 inches. The actual rainfall has been 2·60 inches, showing an excess of 0·34 inch.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

ON THE ESTIMATION OF ALKALINE HYDRATES AND CARBONATES IN THE PRESENCE OF ALKALINE CYANIDES.

By J. E. CLENNELL, B.Sc.,
Chief Chemist, Rand Central Ore Reduction Company,
Johannesburg, S. Africa.

It is frequently a matter of technical importance to estimate rapidly, and with sufficient accuracy for practical purposes, the percentage of alkaline hydrate and carbonate present in the solutions of potassium or sodium cyanide used for the extraction of gold and other purposes.

The ordinary alkalimetric methods cannot be directly applied, owing to the circumstance that the cyanides of the alkali metals behave towards the ordinary indicators, such as litmus, methyl-orange, and phenolphthalein, as though the alkali metal were present as hydrate. A solution of a pure cyanide is alkaline to all these indicators, and remains alkaline, when titrated with hydrochloric acid, until the whole of the alkali metal has been converted into chloride, as in the following equation:—

$$KCy + HCl = HCy + KCl.$$

Thus 10 c.c. of a 0·53 per cent solution of pure potassium cyanide were titrated with normal hydrochloric acid, using phenolphthalein as indicator. It was found that 0·8 c.c. were required to destroy the pink colour of the solution. As 1 c.c. of normal hydrochloric acid corresponds with 0·065 grm. KCy, this indicates a percentage of 0·52 KCy in the solution.

Ten c.c. of a 0·45 per cent solution of commercial potassium cyanide were titrated with half-normal hydrochloric acid, using phenolphthalein as indicator. It was found that 1·35 c.c. of acid were required. Calculating as before, this indicates the presence of 0·044 grm. potassium cyanide, or 0·44 per cent in the solution.

In two experiments 20 c.c. of a 0·455 per cent solution of commercial potassium cyanide were titrated with decinormal hydrochloric acid. The end-point of the phenolphthalein reaction was much more indefinite and difficult to observe than when normal and half-normal solutions had been used, and was obtained in the two experiments at 13·9 and 14·1 c.c. of N/10 hydrochloric acid respectively. Taking the mean of these, 14 c.c. corresponds to 0·091 grm. KCy, indicating a strength of 0·455 per cent.

After the disappearance of the colour with phenolphthalein, the solution still appeared alkaline to methyl-orange. In the titration with half-normal acid described above, it was found that an additional 0·1 c.c. (in all 1·45 c.c.) was necessary to complete the reaction when a drop of methyl-orange was added to the colourless liquid. This corresponds to 0·047 grm. KCy, or 0·47 per cent, as against 0·45 per cent theoretical.

In the titration with decinormal hydrochloric acid, the end-point with methyl-orange as indicator was obtained with 15·2 and 15·1 c.c. respectively, thus indicating a percentage of 0·472 against 0·455 per cent theoretical. The higher values obtained with methyl-orange as indicator are due, as will be shown later, to a small quantity of carbonate existing in the alkaline cyanide.

In March, 1894, some experiments were undertaken by the writer to devise a method of estimating the amount of caustic alkali in cyanide solutions. It was found that when nitrate of silver is added to the solution in sufficient quantity to produce a permanent turbidity, the alkalinity may be rapidly and accurately estimated by titrating the slightly turbid solution with hydrochloric acid, using phenolphthalein as indicator. The double cyanide of silver and an alkali metal formed by the addition of silver nitrate to the alkaline cyanide is not alkaline to phenolphthalein. This was verified by the following experiments:—

a. A mixture was made consisting of 10 c.c., 0·53 per cent, potassium cyanide, and 10 c.c. of a solution of sodium hydrate, of which 1 c.c. was equivalent to 0·945 c.c. normal hydrochloric acid.

This mixture was first titrated with silver nitrate, 5·3 c.c. of the standard solution being required to produce a permanent turbidity. The silver nitrate solution was of such a strength that 1 c.c. = 0·01 grm. KCy. A drop of phenolphthalein was added, and the liquid titrated with normal hydrochloric acid. It was found that 9·4 c.c. were required (theoretical 9·45 c.c.).

b. 20 c.c. of 0·535 per cent cyanide solution were taken.

Silver nitrate was added in sufficient quantity to just produce a turbidity. The liquid was then titrated with decinormal hydrochloric acid, and phenolphthalein indicator. The quantity required was 2·5 c.c. N/10 hydrochloric acid. The colour of the indicator disappeared rather slowly towards the end of the reaction. This quantity (2·5 c.c.) may be taken to represent the amount of alkali (hydrate and carbonate) present in 20 c.c. of the solution of commercial cyanide used in this and the following experiments. It must be remembered that in titrating a carbonate with phenolphthalein as indicator, the value obtained represents the quantity of acid required to convert the carbonate into bicarbonate, corresponding to the equation—

$$K_2CO_3 + HCl = KCl + KHCO_3,$$

whereas with methyl-orange the number represents the quantity of acid required to convert the carbonate into chloride (*i.e.*, twice the quantity required with phenolphthalein) as follows:—

$$K_2CO_3 + 2HCl = 2KCl + CO_2 + H_2O.$$

c. A mixture was made of 20 c.c. of the same 0·535 per cent cyanide solution, and 10 c.c. decinormal caustic potash solution.

This was titrated first with silver nitrate, 10·95 c.c. being required to give a permanent turbidity. A few drops of phenolphthalein were added, and the solution titrated with N/10 hydrochloric acid. 12·65 c.c. of the latter were required. Subtracting the 2·5 c.c. corresponding with the alkali present in the cyanide, we have 10·15 c.c. (by theory 10 c.c.) representing the alkalinity of the caustic potash.

Addition of silver nitrate in excess of the amount required to give a permanent turbidity did not appear to affect the result, except in so far that the dense white precipitate of silver cyanide obscured the end-point of the colour reaction.

a. A mixture was made of 20 c.c., 0·535 per cent, potassium cyanide, and 10 c.c. decinormal caustic potash.

To this, 20 c.c. of the standard silver nitrate solution were added (*i.e.*, more than sufficient to convert KCy into $KAgCy_2$, but not sufficient to precipitate all the cyanogen as AgCy.

This mixture was titrated with N/10 hydrochloric acid, and phenolphthalein indicator. 12·55 c.c. were required.

Deducting 2·5 c.c. as before, we have 10·05 c.c. (against 10 c.c. theoretical) representing the alkalinity of the caustic potash.

b. A mixture was made of 20 c.c., 0·535 per cent, potassium cyanide, and 10 c.c. decinormal caustic potash.

To this, 25 c.c. of the standard silver nitrate was added (*i.e.*, more than sufficient to convert the whole of the cyanogen into AgCy). The precipitate was very dense and brown from presence of silver oxide, formed by the action of the caustic potash on the excess of silver nitrate. During the subsequent titration this brown tint disappeared, but towards the end of the reaction was succeeded by a purplish tint, which made the final point difficult to observe. It was found that 12·2 c.c. of N/10 hydrochloric acid were required to destroy the phenolphthalein colour. Deducting 2·5, we have 9·7 c.c. (against 10 c.c.) indicating the alkalinity of the caustic potash.

It is noteworthy that the presence of caustic alkalis, or the addition of the same to the cyanide solution before titration, does not affect the accuracy of the estimation of cyanide by means of silver nitrate. Moreover, the turbidity produced by the silver cyanide is not removed by the addition of moderate quantities of alkaline hydrate of ordinary strength.

When alkaline carbonates are present, they may be estimated as follows:—The solution is titrated with hydrochloric acid, using methyl-orange as indicator. The number obtained is the equivalent of the total alkali present (whether as cyanide, carbonate, or hydrate). The quantity of cyanide may be estimated in another portion of the solution by titration with silver nitrate, and its equivalent in hydrochloric acid deducted from the value obtained by the first titration. After the estimation of the cyanide as above, the same portion of solution may be titrated with N/10 hydrochloric acid, using phenolphthalein as indicator.

Methyl-orange cannot be used for this purpose, as the turbidity masks the delicate change of tint, marking the end of the reaction.

The indication with phenolphthalein gives the equivalent in hydrochloric acid of the hydrate + half the carbonate (see above).

These results were confirmed by the following experiments:—

a. A solution of potassium carbonate was prepared such that 100 c.c. required 9·7 c.c. normal hydrochloric acid to produce neutrality with methyl-orange as indicator. A solution of potassium cyanide was prepared containing 0·53 per cent. It was found that 100 c.c. of this solution required 10 c.c. of normal hydrochloric acid to give the indication with methyl-orange.

The following mixture was made:—10 c.c. of the above cyanide solution, and 50 c.c. of the above potassium carbonate solution.

On titrating the mixed solution with normal hydrochloric acid, it was found that 5·8 c.c. were necessary to give the methyl-orange indication (by theory 5·85).

b. The following mixture was made:—10 c.c. of the above cyanide solution, 50 c.c. of the above carbonate solution, and 10 c.c. of a solution of caustic soda such that 10 c.c. = 9·6 c.c. normal hydrochloric acid.

This was titrated with normal hydrochloric acid, using methyl-orange as indicator. It was found that 15·5 c.c. were necessary. By theory:—

Equivalent of cyanide	=	1·0 c.c.
,, potassium carbonate .	=	4·85 ,,
,, caustic soda	=	9·6 ,,
Sum of equivalents	=	15·45 ,,

c. The following solutions were prepared:—

Potassium Cyanide, 0·455 *per cent.*—Hydrochloric acid equivalent of 10 c.c. with phenolphthalein = 6·75 c.c. N/10 HCl; with methyl-orange = 7·25 c.c. N/10 HCl.

Sodium Hydrate.—Hydrochloric acid equivalent of 10 c.c. with phenolphthalein = 9·1 c.c. N/10 HCl; with methyl-orange = 9·45 c.c. N/10 HCl (the difference being due to carbonate present in the solution).

Sodium Carbonate.—Hydrochloric acid equivalent of 10 c.c. with phenolphthalein = 5·15 c.c.; with methyl-orange = 10·35 c.c.

A mixture was made containing 200 c.c. of the above potassium cyanide, 10 c.c. of the above sodium hydrate, and 10 c.c. of the above sodium carbonate.

Calculating from the above values, 10 c.c. of the mixture should be equivalent, with phenolphthalein, to 6·8 c.c. N/10 hydrochloric acid; with methyl-orange, to 7·5 c.c. N/10 hydrochloric acid.

20 c.c. of the mixture were titrated with decinormal hydrochloric acid. The indication with phenolphthalein (which was observed with some difficulty) was obtained at 13·5 c.c. (theoretical = 13·6 c.c.). On adding methyl-orange and continuing the titration, the end-point was reached with 15·2 c.c. (theoretical 15 c.c.).

d. The following solutions were prepared:—

Potassium Cyanide, 0·548 *per cent.*—When this solution was titrated with N/10 hydrochloric acid, with phenolphthalein indicator, after addition of silver nitrate to produce a permanent turbidity, 1·25 c.c. of acid were required for every 10 c.c. of the cyanide solution indicating alkaline hydrates or carbonates.

Potassium Hydrate.—10 c.c. = 9·9 c.c. N/10 HCl, with phenolphthalein indicator.

Potassium Carbonate.—10 c.c. = 4·1 c.c. N/10 hydrochloric acid, with phenolphthalein indicator.

The following mixture was made:—20 c.c. of the above cyanide solution, 10 c.c. of the above potassium hydrate solution, and 10 c.c. of the above potassium carbonate solution.

This was first titrated with silver nitrate, 10·95 c.c. being required to produce a permanent turbidity. A few drops of phenolphthalein indicator were then added, and the titration continued with N/10 hydrochloric acid, of which 16·4 c.c. were necessary to complete the reaction. By theory:—

20 c.c. of the cyanide	=	2·5	c.c.	N/10 HCl.
10 ,, hydrate	=	9·9	,,	,,
10 ,, carbonate ..	=	4·1	,,	,,
Sum of equivalents ..	=	16·5	,,	,,

The above experiments are sufficient to show that the amount of cyanide, hydrate, and carbonate in a given solution may be estimated, with enough accuracy for practical purposes, from the three following determinations, each of which is rapidly made without demanding any special degree of skill or technical knowledge on the part of the operator.

1. Estimation of the cyanide by direct titration with silver nitrate.
2. Estimation of hydrate + half the carbonate by adding phenolphthalein to the same solution and continuing the titration with hydrochloric acid.
3. Estimation of total alkali by direct titration with hydrochloric acid, using methyl-orange as indicator.

The writer has great pleasure in acknowledging his indebtedness to his friend Clarence A. Seyler, B.Sc., for valuable assistance and suggestions in devising and executing the experiments described above; and to Dr. Morgan, Public Analyst, Swansea, for kindly allowing the use of his laboratory for carrying out these researches.

Royal Institution.—The Right Hon. Lord Rayleigh, F.R.S., Professor of Natural Philosophy in the Royal Institution, will deliver a course of six experimental lectures on "Waves and Vibrations" at the Royal Institution, on Saturdays, March 2, 9, 16, 23, 30, and April 6. His Lordship will also deliver the Friday Evening Discourse on April 5th, when his subject will be "Argon: the New Constituent of the Atmosphere."

REMARK ON THE RESEARCH OF CURTIUS AND DADICHEN: "SYNTHESES OF BENZENEHYDRAZINES BY MEANS OF HYDRAZINHYDRATE."

By A. PURGOTTI.

In the above-named memoir, received by the editor of this Journal on July 25 and published on September 15, the authors, along with other researches, made known their observations on the action of hydrazinhydrate upon 1, 2, 4-chlordinitrobenzene and 1, 2, 4, 6-chlortrinitrobenzene, and described the 1, 2, 4-dinitrophenylhydrazin as well as the 1, 2, 4, 6-trinitrophenylhydrazin along with some derivatives.

The authors above named were doubtless not acquainted with my first preliminary communication "Sull' azione dell' idrato d'idrazina sul chloruro di picrila" ("On the Action of Hydrazin upon Hydrazinhydrate upon Picryl Chloride"), which had been sent to the editor of the *Gazetta Chimica Italiana* on December 29, 1893, and was published on March 15, 1894. In that communication I described the 1, 2, 4, 6-trinitrophenylhydrazin, and reserved to myself to publish further results on the same question and on the chlornitrobenzene. In like manner Curtius and Dadichen have not been aware of my memoir "Sulla 2, 4-dinitrofenilidrazina a sulla picril-idrazina a loro derivati" ("On 2, 4-Dinitrophenylhydrazin and on Picrylhydrazin and their Derivatives"), which were sent in to the *Gazetta Chemica Italiana* on May 9, was announced in the issue for the same month, and was published July 4 of that year.

In this research I arrived at the same conclusions as Curtius and Dadichen, and among the various derivatives I described the condensation product of picrylhydrazin with acetacetic ester—a product which the above authors have not obtained.

From the above dates the priority of the synthesis of 1, 2, 4-dinitrophenylhydrazin and of 1, 2, 4, 6-trinitrophenylhydrazin by means of hydrazinhydrate is manifest. —*Journal für Praktische Chemie*, N.S., li., Part 1 and 2, p. 111.

ON THE FORMATION OF HYDRAZIN IN AN INORGANIC MANNER.

By P. DUDEN.

Since the discovery of hydrazin by Curtius and Jay in 1889, a series of methods for obtaining this interesting product have been published by them, as well as by Thiele and Von Pechmann.

All these methods have the common feature that they take a circuitous way through nitrogenous organic substances. They set out from such aliphatic carbon compounds as contain a diazo-nitrosamin or nitramin group, combined with a carbon-complex which may be easily split off. The formation of hydrazin is effected either by direct reduction or by reduction followed by the hydrolytic scission of the primary amido-product formed.

Attempts have been made to transfer this reaction to the inorganic region or to arrive at hydrazin by proceeding from simple purely inorganic nitrogen compounds. It appears, however, that the nearest attempts, such as the reduction of nascent nitrogen or nitrous oxide, or the catenation of the amido-groups of hydroxylamine and ammonia, or the use of metallic ammonium compounds containing an amido-group, do not lead to the desired end.

On the contrary, I have made some experiments with the potassium salts discovered by Fremy and more closely examined by Raschig, and arising on the reaction of sulphurous acid with potassium nitrite. I have observed that nitric oxide potassium sulphite, $K_2SO_3N_2O_2$, on cautious reduction in an alkaline solution, yields hydrazin. Hence by means of this purely inorganic salt it is possible to transmit nitrogen into hydrazin.

This salt, discovered by Davy, has been examined some years ago by Divers and Haga (*Journ. Chem. Soc.*, 1885) as to its behaviour with reductive agents. According to their observations, by reduction with sodium amalgam in a concentrated alkaline liquid it is substantially converted into potassium hyponitrite and potassium sulphite according to the equation—

$$SO_3KN_2O_2+H_2=SO_3KH+2KNO.$$

There is a simultaneous formation of hydroxylamine and ammonia.

If this reduction is effected in the cold with sodium amalgam or zinc powder and ammonia (or soda-lye), we obtain a strongly reductive solution which after acidulation contains a hydrazin salt. There is therefore formed along with hyponitrite the reductive product corresponding to nitric-oxide potassium sulphite, the formation of which, according to Raschig's formula, may be shown as—

$$\begin{matrix}KSO_3\\KO\end{matrix}\!>\!N.NO+H_6=\begin{matrix}KSO_3\\H\end{matrix}\!>\!N.NH_2+H_2O+KOH=$$
$$=H_2N.NH_2+K_2SO_4.$$

The intermediate product first formed could not be more closely examined, as on shaking up with benzaldehyd it yields no sparingly soluble benzaldehyd compound.

In effecting this reaction the nitric oxide freshly prepared is suspended in ice-water, and whilst being refrigerated it is gradually mixed with amalgam in slight excess until a specimen of the liquid strongly reduces Fehling's liquid, and after acidulation and heating, benzalazin separates out on the addition of benzaldehyd. The product thus obtained, $C_{14}H_{12}N_2$, melts at 93°, and has the properties and composition of benzalazin.

With sulphuric acid it yields hydrazin sulphate at 256°. Instead of amalgam we may use other reductive agents acting in alkaline solutions. The production of hydrazin is not sharp, as other reduction products are formed simultaneously.—*Berichte*, xxvii., p. 3498.

THE ACTION OF ALKALIS UPON ORTHO-NITROPHENYLHYDRAZIN.

By E. NIETZKI and E. BRAUNSCHWEIG.

Some years ago one of the present writers attempted to obtain hydrazin from a nitrised phenylhydrazin. The material used was orthonitrophenylhydrazin sulph-acid.

On boiling with alkali-lye it evolved not a trace of hydrazin, and the experiments were abandoned. Dr. Grandmougin, however, who had arrived at a similar negative result, sent us a specimen of a finely crystalline body which he had obtained on supersaturating the aniline liquid with an acid.

As the examination of the present sulpho-acid gave no insight into the constitution of the compound which evidently belonged to a new class of substances, we endeavoured to obtain the simplest representative of this class, and used as our initial material Bischler's orthonitrophenylhydrazin.

Azimidal.—Orthonitrophenylhydrazin if heated is very quickly attacked by alkaline lyes, and even by aqueous ammonia. It dissolves, the liquid becomes nearly decolourised, and on supersaturation with an acid the product of the reaction separates out in needles nearly colourless. On crystallisation from dilute alcohol the new substance is obtained pure, of the composition $C_6H_5N_3O$, having the melting-point 157°. It had been formed by the elimination of water from nitrophenylhydrazin. It has the properties of a somewhat powerful acid. It forms with alkalis salts easily soluble, but with alkaline earths and the heavy metals salts which are in general more sparingly soluble. The lead salt—

$$(C_6H_4N_3O)_2Pb$$

crystallises very readily. If crystallised from hot water it forms colourless shining leaflets which deflagrate at 270°.

It is characterised by great stability and slight tendency to reactions. Acetic anhydride is without action. Nor is it attacked by reductive agents, a proof that the nitro-group is not present as such.

Iodethyl has no action even at a rather high temperature. On heating the lead salt with this reagent in a closed tube, there was at first no result, but a reaction set in when the temperature was raised to 180°. The contents of the tube were coloured brown by the liberation of iodine. They were diluted with alcohol and separated from lead iodide. On evaporating the solution there appeared dark shining crystals of a metallic lustre.

The substance had a strong odour of iodine, gave off violet vapours at a gentle heat, and displayed all the properties of the periodides often obtained from the iodides of the ammonium bases. The iodide was converted into a chloride by treating the alcoholic solution with precipitated silver chloride. The chloride is very soluble both in water and alcohol. It does not crystallise and therefore the platinum double salt was prepared. It forms a yellow crystalline precipitate, $(C_{10}H_{14}N_3Cl)_2PtCl_4$, a remarkable instance of a salt free from oxygen. The new base must have arisen from the original compound by the exit of an atom of oxygen and the introduction of two ethyl groups. All the properties of the base show the presence of a quaternary ammonium group.

If we take away from a chloride of the formula $C_{10}H_{14}N_3Cl$ (as in the double platinum salt) one molecule of ethyl chloride and another ethyl group, we arrive at a compound $C_6H_5N_3$. Such is Ladenburg's azimidobenzol,

If the new substance is a derivative of azimidobenzol, we may conjecture that it may be formed by ethylisation. Azimidobenzol, obtained according to Ladenburg's directions from orthophenylendiamine, was heated to 150° in a sealed tube with iodethyl and one molecule sodium ethylate.

If the alcoholic solution of the product of the reaction is mixed with solution of iodine, crystals are separated which have the appearance and behaviour of the periodide above mentioned, and after being freed from iodine yield a platinum double salt as above described.

Hence a derivative of azimide was formed from the substance just described with a removal of oxygen.

Evidently the original substance in view of its properties and formation must be a hydroxyl derivative. We propose for substances of this class the name of "azimidoles."

As the hydrogen of these bodies is easily replaced by metals, we may understand that on exchanging them for hydroxyl substances of strongly acid properties are formed.

A subsequent analysis of the above-mentioned periodide shows that it contains no oxygen.

If nitrohydrazinsulph-acid is heated with an excess of soda-lye, it congeals on cooling to a paste of colourless needles, a bi-sodium salt, $C_6H_3N_3Na_2SO_4 + H_2O$.

Azimidosulph-acid is hence bibasic.—*Berichte*, xxvii., p. 3381.

Royal Victoria Hall, Waterloo Road, S.E.—At the British Association last autumn, much excitement was caused by the announcement that Lord Rayleigh and Prof. Ramsay had discovered a new element in the air. Their investigations will form the subject of one of the well-known popular lectures at the Royal Victoria Hall, on Tuesday, February 26, at 8.30. It is a "sign of the times" that the newest scientific discoveries are expounded to the public at an admission fee of one penny.

THE SECRET OF THE BROWNIAN MOVEMENTS.*

By R. MEADE BACHE.

(Continued from p. 84).

Heat I applied in various ways, either irregularly or in an endeavour to distribute it as equally as possible on the glass slide on which the particular experiment was made. Mere currents are set up during the adjustment of temperature from radiation. At the same time one can observe and differentiate the motions due to the brownian movements, the motions along currents, and also the motions from terrestrial gravity, if any, exhibited by particles, if the specific gravity of the substance be great, and the microscope be set at an angle with the vertical.

Cold I also applied, putting the slides with their cover-glasses in a freezing mixture of broken ice and water, and reducing them to a very low temperature. Still the movements went on as apparently unmodified as ever. Herr Exner says it will be remembered that glycerin, which under ordinary conditions shows absolutely none or almost no molecular movement, shows it clearly when warmed up to the temperature of 50° C. In all the finely divided bodies, however, which I examined, there seemed to be no increase or diminution in the intensity of the movements, corresponding with their alternate subjection to heat and cold. There were occasions in which I thought that I observed acceleration from light, but I always ended by imputing it to the force of imagination, and if it were not justly ascribable to that cause, the fact that it could be so ascribed is proof positive that if, through the influence of light and heat, any intensification of the movements of the particles took place, it must have been very small. Moreover, the evidence is certainly here to show that even if the movement were intensified by light or heat, that was the only influence that could be ascribed to them, that light and heat could not be deemed the cause of the movement. And lastly, Herr Wiener's micrometric measurements of the range of movement at different temperatures completely bore out this conclusion.

The theory of Herr Wiener that the movements are due to the action of the red wave of light and heat is refuted by the single fact that, as I have proved by experiment, one may interpose at pleasure between the source of light or heat and the particles either a violet glass or a red glass without being able to observe the slightest alteration in the movements, either as to their range or their velocity. That is to say, red rays may be either partially excluded or selectively admitted without diminishing or increasing the liveliness of movement. Hence light can have nothing to do with the phenomenon under discussion, and I have just shown, through the citation of the freezing mixture experiment, that heat can have nothing to do with it.

I have reserved to the very last the discussion of the question as to whether or not the shock, if any there be, from evaporation can have anything to do with the movements, although this was a point that entered into my first investigations. I have reserved it to the last, because its discussion requires more than the brief space which I have devoted to the previous individual results, and because it leads directly to the conclusion that I have finally reached as to the true cause of the movements. I started out with the conception, which it seems is common to everyone, that evaporation might be accompanied with a series of minute explosions, which produce shocks that manifest themselves through the mass of an aqueous solution in the form of minute movements of finely divided matter held in unstable equilibrium by suspension

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* Read before the American Philosophical Society, April 20, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

in the fluid, and that these, escaping cognisance from any ordinary observation, might be visible as such, or in their effects, through the instrumentality of high powers of the microscope. I had come to believe long before, from observation and experiment, that no tremors from mechanical agency or any other, except perhaps from evaporation, could produce the peculiar movements known as brownian, and finally it remained to discover if this or any other intrinsic cause were at work that would account for them.

At this point I encountered an obstacle. My high powers of the microscope were both water-immersion lenses. It seemed, therefore, that even when I had had the drop of liquid under observation, sealed beneath a cover-glass, I might have included, by the use of the water-immersion lens itself, an evaporating surface which might have produced the optical illusion of the movement of the particles in suspension. I proceeded, however, with my experiments upon the assumption that this, as the event proved to be the case, was not true, and meanwhile procured from Vienna a one-fifteenth dry-lens by Reichert, the highest power of dry-lens that he makes.

I had already obtained for high-power lenses a film of liquid thin enough to be observed through all its strata, free of air within the cell, and protected from evaporation by being hermetically sealed. Any ordinary manufactured cell is too deep, and with all precautions taken contains a little air. On the other hand, the mere cover-glass superposed on a glass slide contains too slight a depth of fluid. I made a cell by using gum-shellac traced in a circlet on a glass slide, which cell, when partially dried, is filled to the brim with the liquid to be observed upon, whereupon the cover-glass is pressed into the yielding gum, thereby expressing the contained air with the superfluous liquid, when the product, dried over night, is fit for use on the following evening. One slide, prepared in this manner and filled with a slightly tinted solution of carmine from cochineal, had been observed upon by me for weeks, with a one-tenth water-immersion lens, and afterwards, upon the arrival of the one-fifteenth dry-lens, was observed upon without showing any variation in the range and vividness of movement of the particles subjected to examination. I have even covered the whole microscope with a pall of thick black woollen cloth, so that not a ray of light could enter it either through the cover-glass or the eye-piece, and then carefully placing the eye close to the eye-piece, have suddenly thrown light upon the cover-glass, when the brownian movement among the particles was perceived in as active play as ever. I have therefore concluded from all these experiments that neither heat nor light, nor electricity, nor magnetism, nor mechanical shock, nor, finally, evaporation, is operative in producing the movements; in a word, that the particles move uninfluenced by these forces. I am therefore constrained to believe, upon the basis of the information that I have obtained in the manner described, that it is not the particles which are moved by their own energy, or moved by any energy directly imparted to them from outside sources, but that it is the fluid that moves them.

If their own energy moves the particles, we should see them at the same time obedient also to the law of gravitation among themselves, manifested as the resultant of whatever forces are in play, whereas, although they must be obedient to the law of gravitation among themselves, its effects, and generally as well those of terrestrial gravity, are so masked as not to be at all perceptible. Now when we consider how minute all of these particles are, and yet that they move apparently unhindered with such constancy and force, it ought to be apparent, I should think, that they have no self-motive power. However erratic the paths of individual particles may be, the likeness among the movements is extraordinary, so almost identical in every case, varying in greatness of range and rapidity only in inverse ratio to the size of the particle, that we cannot conceive of self-actuated particles so behaving; for relative greatness of size in self-actuated particles ought to coincide with relatively greater, not relatively less, energy of movement; whereas here the case is reversed. But there are other facts that I have observed through experiment which also prove what I say. In alcohol and, as far as my experiments go, in fixed and volatile oils, the brownian movements are not observable, and yet the microscope plainly reveals that the movements of foreign bodies in all these is as free as in aqueous solutions, and I think more so. So molecular movements of solid particles in suspension in aqueous fluids must take place perforce of the constant repulsions of the constituent molecules of the particular liquid present—water. The minute drops of oils supernatant on water, some of them no larger than the particles in the water below, observed by Dr. Brown, as he says, to be almost or wholly motionless, so behave because the molecules of water glide by the molecules of a substance for which they have not even the affinity that would compass opposition. Be the globules of oil on water never so small or large, the molecules of the aqueous fluid glide by them. Whether a small or a large globule of oil be the particle itself on water, there is no movement of the particle. Dr. Brown says none, or almost none. I think that he was mistaken, that there is no molecular movement whatever.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 7th, 1895.

Dr. ARMSTRONG, President, in the Chair.

MESSRS. W. Herbert Walden, Robert H. Wilson, and J. Young were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Eugen Blume, Russell Ho., Trinity, Edinburgh; Virgil Coblentz, Ph.D., M.A., 115 W. 68th Street, New York, U.S.A.; John Francis Hutchins Gibbard, 362, Mare Street, Hackney; Alexander Gunn, 66, Finsbury Park Road, N.; Evan Lewis Jones, B.A., 4, Bank Buildings, Llandilo; John McGlashan, Cawnpore Sugar Works, Cawnpore, India; Lama Gray Patterson, Washington, Pa., U.S.A.; Thomas Coke Squance, M.D., M.S., &c., 4, Beauclerc Terrace, Sunderland; Alfred F. Theodosius, B.A., Magdalen College School, Oxford; George John Ward, The Cottage, Hallam Fields, Ilkeston.

Of the following papers those marked * were read:—

*12. "*The Action of Heat on Ethylic β-amidocrotonate.*" Part II. By J. NORMAN COLLIE, Ph.D.

In Part I. of this paper the author has shown that when ethylic β-amidocrotonate is heated it condenses to form a pyridine derivative, ethylic lutidone-monocarboxylate. He has since found that at least three other nitrogenous condensation products are formed when the amidocrotonate is destructively distilled.

The compound which is formed in largest quantity is ethoxylutidine (*αγ*-dimethyl-*α'*-ethoxypyridine),

$$2C_6H_{11}NO_2 = C_9H_{13}NO + NH_3 + CO + CO_2 + C_2H_4.$$

It is a pleasant-smelling liquid, b.-p. 217—218° (corr.). It forms a platinum salt, which melts at 226° (corr.) with much decomposition. When heated in a sealed tube with fuming hydriodic acid, ethylic iodide and pseudolutidostyril are produced.

A dimethylpyrrol is also formed in small quantities,—

$$2C_6H_{11}NO_2 = C_6H_9N + 2CO_2 + 2C_2H_4 + NH_3 + H_2.$$

This dimethylpyrrol seems to be identical with one which was obtained by Ciamician and Wiedel by destructively distilling gelatin. Its boiling point lies between 170°

and 175°. It has also been obtained by Knorr by reducing isonitroso-ethylic β amidocrotonate.

A third substance has been isolated which is also doubtless a pyridine derivative. It is produced by the following reaction:—

$$2C_6H_{11}NO_2 = C_6H_8N_2O + EtOH + CH_3COOEt.$$

When heated with zinc-dust, it gives α-picoline. It contains a hydroxyl group, for it yields a monochloride with pentachloride of phosphorus. It is probably either α-methyl-γ-amido-α′-hydroxypyridine or α-methyl-α′-amido-γ-hydroxypyridine. It does not diazotise when acted on with fuming hydrochloric acid and sodium nitrite, but with nitrous fumes in aqueous solution it forms a curious addition product:—

$$C_6H_8N_2O + NO_2 + H_2O = C_6H_{10}N_3O_4.$$

*13. "*The Acidimetry of Hydrogen Fluoride.*" By T. Haga and Y. Osaka.

The authors have separately examined the behaviour of the usual indicators in the neutralisation of hydrofluoric acid. That its alkali salts blue litmus, and that its avidity number places it among the vegetable acids rather than with the strong mineral acids, appear to be the only two facts yet recorded bearing upon its acidimetry.

To get uniform indications it was found necessary to have not only the acid pure, but the titrating solutions also; a little silica, alumina, or carbon dioxide affecting the titration more than it would in the case of the ordinary mineral acids.

Phenolphthaleïn is the best indicator, and leaves nothing to be desired when potash or soda is used for the titration. *Rosolic acid* is almost equal to it, and can be used besides with ammonia. With both indicators the change of colour has the advantage of being very evident in platinum vessels.

Both *cochineal* and *brazil-wood* infusions give satisfactory results. Brazil-wood paper shows alkalinity before all the acid is neutralised, and cannot, therefore, be used. *Turmeric paper* gives fairly good results. *Methyl orange* is useless.

Litmus, *lacmoïd*, and *phenacetolin* are all capable of being made to yield accurate results in the hands of an experienced person. Some peculiarities in the behaviour of litmus are described in the paper which suggest the conclusion that the molecule of hydrogen fluoride may be H_3F_3 or H_4F_4.

*14. "*Composition of Ancient Silver Ornaments from Peru.*" By Miss C. Walker.

The two ornaments examined were found in the ancient graves of Incas, at Chimbote, and they were analysed in the Chemical Laboratory of the University of Virginia. Both ornaments were covered by a thin crust, chiefly composed of silver chloride and a basic copper carbonate in the one case, and of cuprous oxide in the other. One ornament was a silver plate composed of 85·24 per cent of silver, 13·96 per cent of copper, and 0·15 per cent of gold. The other ornament was a ring, joined by soldering the ends of a flat metallic band. This consisted of 25·51 per cent of silver, 72·09 per cent of copper, 0·25 per cent of gold, 1·21 per cent of iron, 0·5 per cent of zinc, and about 0·1 per cent of lead. The iron, lead, and zinc were probably derived from the solder.

It would seem that these ornaments had been made from native silver.

*15. "*Molecular Change in a Silver Amalgam.*" By Miss F. T. Littleton.

When an amalgam of silver and mercury is moderately heated, considerable swelling takes place, suggestive of the escape of gas, and, on cooling, the pasty mass sets to a hard crystalline porous substance. The increase in volume is most considerable when the metals in the amalgam are present in the proportions corresponding with the formula $AgHg_4$.

On examining the action it is found that no appreciable quantity of gas escapes from the amalgam, and the swelling must therefore be attributed to the molecular changes which accompany the union of the two metals.

16. "*Sulphocamphylic Acid.*" II. By W. H. Perkin, jun.

At the commencement of this investigation in 1891 a number of analyses of sulphocamphylic acid were carried out, as mentioned in the previous communication (*Proc.*, 1893-94, p. 110), and the author then observed that at a temperature of 110—115° this acid has the composition $C_9H_{14}SO_5$ or $C_8H_{12}(SO_3H)\cdot COOH$, the crystals of the acid which separate from aqueous solution being $C_9H_{14}SO_5 + 3H_2O$; this observation has since been confirmed by Koenigs and Meyer (*Ber.*, 1894, 3466).

That this formula correctly represents the composition of sulphocamphylic acid is shown by the analysis of its sulphobromide, $C_8H_{12}(SO_2Br)\cdot COOH$, which the author has succeeded in preparing by the interaction of the potassium salt of the acid and phosphorus pentabromide. This derivative crystallises from dilute methyl alcohol in prisms; it melts at 152°, and at a slightly higher temperature decomposes, evolving sulphur dioxide. By extracting the black residue with light petroleum, and re-crystallising the product from formic acid, a colourless crystalline acid, $C_8H_{12}Br\cdot COOH$, is obtained—

$$= C_8H_{12}(SO_2Br)\cdot COOH - SO_2.$$

This new acid melts at 130°—132°, and is readily acted on by alcoholic potash, being converted into an acid of the composition $C_8H_{11}\cdot COOH = C_8H_{12}Br\cdot COOH - HBr$. This acid, which melts at about 105°, may possibly be identical with the acid of this composition (m.-p. 108°), which is formed when sulphocamphylic acid is fused with soda (see below).

The author has continued his experiments on the fusion of sulphocamphylic acid with potash and soda, and finds that in all cases the product contains two isomeric unsaturated acids, $C_8H_{11}\cdot COOH$ (m.-p. 108° and 148), which can be separated only with great difficulty by re-crystallisation, but which were finally obtained in a pure condition by taking advantage of the fact that the aqueous solution of the ammonium salt of the higher melting acid dissociates readily at 80°, the acid separating, whereas the ammonium salt of the acid of melting-point 108° remains unchanged at this temperature.

The acid melting at 148° has already been obtained by Kachler (*Annalen*, clxix., 133); it is readily acted on by bromine, hydrogen bromide being evolved, and is converted into a crystalline acid, $C_8H_{10}Br_3\cdot COOH$, which melts at 178°.

The isomeric acid melting at 108° is also readily attacked by bromine, but no hydrogen bromide is evolved, and it yields, on oxidation with permanganate, a syrupy hydroxy-acid.

A careful investigation of these new compounds, as well as of those mentioned in the previous communication, is in progress.

17. "*Derivatives of Ethyl-orthotoluidine.*" By W. MacCallum, jun.

This paper contains an account of work conducted in the year 1893, at Mülhausen, by the late Mr. William MacCallum, jun. The account now given has been drawn up from Mr. MacCallum's notes by Dr. Hepburn. The object of the investigation was to ascertain whether nitrosoethyltoluidine and the diazoamido-derivatives of nitroethyltoluidine could be converted into ethylisindazole and nitroethylisindazole respectively. This proved not to be the case, but in the course of the investigation several new compounds were prepared, amongst them being *nitroethylorthotoluidine*, *ethyl toluylenediamine*, *nitroethylacetoorthotoluidine*, m-*nitroethylnitrosoorthotoluidine* and *ethyldiazoamidotoluene*. The last-named compound furnishes the same nitro-indazole as is formed by diazotising *m*-nitrotoluidine and heating the product with dilute sulphuric acid.

18. "*Acetyl Derivatives of Benzaconine and Aconitine.*" By Wyndham R. Dunstan, F.R.S., and Francis H. Carr.

The authors have made a number of experiments in the hope of being able to convert benzaconine into aconotine by introducing an acetyl group into it. These experiments have so far been unsuccessful, but several new compounds have been obtained, both from benzaconine and from aconitine, the analyses of which serve to further confirm the formulæ which the authors have previously proposed for these alkaloids, $C_{31}H_{43}NO_{11}$ and $C_{33}H_{45}NO_{12}$, whilst the analytical results do not bear out the formulæ proposed by Freund and Beck, $C_{32}H_{45}NO_{10}$ and $C_{34}H_{47}NO_{11}$. By acting on benzaconine dissolved in chloroform with acetic anhydride during 24 hours at the ordinary temperature an amorphous base is obtained which forms crystalline salts; the *hydrobromide* melts at 265°. The substance does not seem to be toxic. When hydrolysed by heating with water in a closed tube it furnishes acetic acid and benzaconine.

At 100°, or by Liebermann's method, a crystalline base (m.-p. 255°—256°) results from the action of acetic anhydride. On hydrolysis this substance breaks up into aconine, benzoic acid, and 24·4 per cent of acetic acid, proving it to be a *triacetyl benzaconine.* This derivative appears to be identical with that described by Freund and Beck as a monacetyl derivative. These observers do not appear to have estimated the amount of acetic acid produced on hydrolysis, but to have trusted to the results of combustions, which, as the authors have previously pointed out, furnish by themselves no safe criteria of composition with such compounds. This base also appears to be non-poisonous.

Acetyl chloride, acting in the cold on benzaconine dissolved in chloroform, produces a crystalline base (m.-p. 162°), which forms crystalline salts, including an aurichloride. It also appears to be a *triacetyl benzaconine,* $C_{31}H_{40}(CH_3CO)_3NO_{11}$.

The further action of acetyl chloride on this substance, or on benzaconine, in a sealed tube at 100° C., results in the formation of a crystalline base (m.-p. 211), which appears to be *tetracetyl benzaconine.* It forms a remarkable colourless aurichlor-derivative (m.-p. 225°).

Acetic anhydride does not act on aconitine.

Acetyl chloride forms *diacetyl aconitine* (m.-p. 158°), which differs from its isomeride triacetyl benzaconine principally in its physiological action, which resembles that of aconitine, and also in the property of forming an aurichlor-derivative, as well as in its crystalline form.

Triacetyl aconitine (m. p. 206—207°) also differs from its isomeride tetracetyl benzaconine in its crystalline form and physiological activity.

Pyraconitine and acetyl chloride interact, forming a crystalline base (m. p. 203°), which is *triacetyl pyraconitine.* This substance does not seem to be poisonous. In determining the composition of each of these substances, reliance has been placed on the determination of the amount of acetic acid formed on hydrolysis. Combustions for carbon and hydrogen have also been made, and the results bear out the formula suggested by the authors for aconitine, and do not agree with the formula suggested by Freund and Beck, as will be seen from the following table, which also includes analysis of aconine and of pyraconitine hydrobromide.

In establishing their new formula for benzaconine ($C_{31}H_{43}NO_{11}$) the authors relied on the determination showing that one molecular proportion of acetic acid is separated when it is formed from aconitine ($C_{33}H_{45}NO_{12}$). The base being amorphous did not lend itself well to the confirmation of this formula, especially as the composition of the alkaloid only differs within the limits of experimental error from that of aconitine. They showed, however, that the percentage of gold in the remarkable colourless aurichlorbenzaconine agrees well with the calculated number. Freund and Beck state that they have been unable to obtain this substance. The authors can only reply that they find no difficulty whatever in producing it, and that one of them, in conjunction with Mr. E. F. Harrison, has now succeeded in converting it into a crystalline aurichloride.

		Freund.	Dunstan and Carr.	
		Calculated.	Found.	Calculated.
		$C_{40}H_{53}NO_{14}$.		$C_{39}H_{51}NO_{15}$.
Triacetyl aconitine,	C.. ..	62·25	60·42	60·54
	H.. ..	6·87	6·82	6·59
		$C_{38}H_{51}NO_{13}$.		$C_{37}H_{49}NO_{14}$.
Diacetyl aconitine,	C	62·55	60·98	60·74
	H.. ..	6·99	7·06	6·70
		$C_{32}H_{43}NO_9HBr$.		$C_{31}H_{41}NO_{10}$.
Pyraconitine hydrobromide,	C	57 65	55·8	55·69
	H.. ..	6·60	6·28	6·28
		$C_{25}H_{41}NO_9$.		$C_{24}H_{39}NO_{10}$.
Aconine,	C.. ..	60·12	57·31	57·48
	H.. ..	8·21	8·02	7·78

19. "*Aconitine Aurichlorides.*" By Wyndham R. Dunstan, F.R.S., and H. A. D. Jowett. B.Sc.

In a previous communication (*Trans.*, 1893) the authors described three modifications of aconitine aurichloride, differing in melting point and apparently in crystalline form, each being produced under different conditions from the amorphous aurichloride and convertible into each other. The α-compound (m. p. 135°) was obtained by crystallising from aqueous alcohol, aqueous acetone, or from a mixture of chloroform and ether; the β-compound (m. p. 152°) was formed by crystallising from strong alcohol, and the γ-compound (m. p. 176°) by crystallising the β-compound from a mixture of chloroform and ether.

Freund and Beck (*Ber.*, xxvii., 724) have stated that the α-aurichloride is really a trihydrate, and that the β-compound is the anhydrous salt; the γ-compound they do not mention. They describe a new salt which they state is an alcoholate, and is obtained by crystallising from absolute alcohol; this salt melts at 135°, and loses its alcohol when heated or left for a long time in the desiccator.

The authors have, therefore, again examined the aurichlorides, and have confirmed their previous results, The α-aurichloride cannot be regarded as a trihydrate, since it contains 19·64 per cent of gold, the formula—

$$C_{33}H_{45}NO_{12},HAuCl_4$$

requiring 19·89 per cent, or, using Freund's formula for aconitine, 19·93 per cent, whereas a trihydrate requires either 18·86 per cent or 18·89 per cent, depending on which formula is taken. On heating at 100—120° during many hours and weighing at intervals, the total loss was much less (2 per cent) than that required for the trihydrate, although the salt had slightly decomposed. After this prolonged heating, the substance still melted very close to its original point.

Moreover, they have now succeeded in producing the α-aurichloride in the absence of water by crystallising from anhydrous acetone.

The authors have also examined the substance which Freund and Beck regard as an alcoholate of aconitine aurichloride. The salt prepared by the method they describe closely resembled the β-aurichloride in appearance. The air-dried salt melted indefinitely between 145—152°, but (after drying at 100°) at 152°. By drying this substance under different conditions the authors find that the loss is variable, but in no case does it amount to the percentage required for an alcoholate—4·46 or 4·47 per cent. They conclude that this substance is merely the β-aurichloride with a small quantity of alcohol still adhering to it; this alcohol is slowly lost when the salt is exposed to air.

Anniversary Dinner.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Hotel Métropole on Wednesday, March 27th, at 6.30 for 7 p.m. It is hoped that as many Fellows as possible will be present.

Erratum.—In the report of the Chemical Society's meeting for Jan. 17th (p. 71, col. 2, five lines from bottom), the formula should read :—$C_{18}H_{3c}O_{14}(N_2HC_6H_5)_2$.

NOTICES OF BOOKS.

Cellulose, an Outline of the Chemistry of the Structural Elements of Plants with reference to their Natural History and Industrial Uses. By Cross and Bevan (C. F. Cross, E. J. Bevan, and C. Beadle). London and New York: Longmans, Green, and Co. 1895. 8vo., pp. 320.

Sparingly reactive as are the celluloses, they yet present to the chemist problems of the greatest interest. We are therefore much indebted to the authors for having brought to a focus the results already reached concerning these compounds, and for indicating—as they do most carefully—how our knowledge of the celluloses may be extended and deepened. The study of their relations with the starches, gums, and sugar leaves room for much good work.

Perhaps still more interesting is the investigation of the celluloses to the physiologist who seeks to trace how these apparently inert bodies are evolved from the constituents of plant-food, and how they in turn are transmuted within the organism. It is interesting to note the existence of cellulose in animals. The authors here raise the question whether animal celluloses—tunicin, &c.,—are elaborated *de novo* in the Ascidia, or if they retain their constitutional features in passing from the vegetable to the animal organism (pp. 87 and 88).

Perhaps the technicist is especially concerned with the morphology, the physiology, and the embryology of cellulose. In the manufactures of textile goods, of paper, of gun-cotton, of various water-proof tissues, and in the arts of bleaching, dyeing, and tissue printing, we can lay no firm foundation without a rational study of plant-fibres. The way in which John Mercer succeeded in giving to cotton tinctorial properties approaching those of animal fibre was truly noteworthy. Still more noteworthy is the manner in which his discovery has been neglected under the most frivolous pretexts.

The authors first discuss the typical cellulose and its group, passing then to its natural compounds, the pecto-celluloses and muco-celluloses, as also the adipo-celluloses and cuto-celluloses. The second group have the characteristic property of forming gelatinous hydrates, approaching those of certain seeds and fruits. But the pectic group have less hydrogen in proportion to the carbon and oxygen than the carbohydrates.

Of the adipo-celluloses cork serves as the type.

The authors show that the elaboration of the compounds in question is, as regards "mass effect," the main work of the vegetable world. They are not aware of any special proof of the assumption that the celluloses are non-nitrogenous *ab initio*. It is at least possible that in the earlier stagss of growth they contain NH_2 residues. They show that the chemistry of the vegetable world, which depends in its proximate relationships upon the polyhydroxy-derivatives of the C_6 unit, is a most striking manifestation of the carbon atom itself.

The third part of the work is devoted to the experimental and applied part of the subject, and should not be entered upon by the student without a previous assimilation of the former parts. The authors give indications for the microscopic examination of the fibres. They recommend the student to sow some flax seed and examine the stem from time to time during the growth of the crop. Experiments are to be made in bleaching, using flax and jute as raw materials. Rapid combustion is to be studied, as also hydration and dehydration, and the effects of solvents, the parchmentising process, and destructive distillation. Next follow methods for the identification of the members of the group.

Bleaching processes are studied as applied to textiles and paper pulp. Under dyeing and printing processes we find a notice of what was until lately a matter of controversy,—the question whether dyeing is a mechanical or a chemical process. The authors regard it as a special case of the transfer of a body—*i.e.*, a tinctorial substance—from one solvent to another. Hence a dyed fibre is a solid solution of the colouring matter in the fibre substance. Attention is called to the "cosmopolitan relationships" of the ligno-celluloses as compared with the celluloses.

A suggestion is thrown out that laundry work should be more definitely organised as a chemical industry.

Notice is taken of the influence of papers, according to the raw material employed, on the permanence of books and documents. The nitro-celluloses, or rather cellulose nitrates, are next considered.

In summing up the authors tell us that the study of the celluloses "is a province of applied chemistry, whereas in many others the distinctions between science and practice exist only in the minds of those who grasp neither the one nor the other."

Had we the power we would have this sentence inscribed on high not only in every technical school but in every chemical works.

The work is enriched with fourteen microphotographs of various fibres.

Our opinion of the book is that it should be found on the bookshelves of every factory, laboratory, or office where fibrous materials are bought, sold, or elaborated.

The Cyanide Process for the Extraction of Gold, and its Practical Application on the Witwatersrand Gold Fields in South Africa. By M. Eissler. London: Crosby Lockwood and Son. 1895. Crown 8vo., pp. 90.

For the appearance of this useful work we are doubtless indebted to the recent litigation on the cyanide process. But we must not suppose that Mr. Eissler has written merely on the spur of the moment. He has spent some years at the South African gold fields, and has enjoyed especial opportunities for a close and practical study of the process. The solubility of gold when in a state of fine division was known, according to the author, "in the middle ages, and the gilding of metals was carried out in those remote days by jewellers and alchemists by the use of gold in cyanide solutions." Here we wish the author had been a little more explicit and informed us how the metallurgists of the past obtained their cyanide. Free cyanogen, according to all the text-books, was discovered by Gay-Lussac. Even Prussian blue and potassium ferrocyanide scarcely date back to the middle ages. But hydrocyanic acid in a dilute and impure state was certainly familiar to the sages and priests of ancient Egypt, and it may have enabled the mediæval alchemists to concoct cyanide solutions capable of dissolving gold. In modern times the cyanide process was first tried on a commercial scale in 1867 in the United States, but was apparently unsuccessful. The first real success, according to our author, was obtained by the McArthur-Forest Company in South Africa. It is estimated by experts that the gold deposit of the Witwatersrand is capable of yielding gold to the value of £215,000,000, of which one-third would not be won without this process.

The treatment is thus summarised: The process is most applicable to tailings, where the ores have already undergone plate amalgamation. The first stage is treatment with an alkaline solution, containing 4 ozs. caustic soda per ton of solution. By this means acids are neutralised, and organic matter is destroyed. Next follows the strong cyanide solution, from 0·3 to 0·5 per cent. of KCy, the quantity run on being one-third the weight of the tailings in the vats. This strong solution is allowed to act for three hours, followed by a gradual drainage for four hours. A weak solution, containing 0·15 per cent. of cyanide, is then run on to wash out the dissolved gold. Lastly comes washing with water to the extent of not less than 7 per cent. The dissolved metal is next deposited upon zinc shavings. The precipitation is influenced by a variety of conditions which have been carefully studied by Mr. W. Bottel, and are here quoted. The same authority has also studied the action of impurities and base metals in ores, which may prevent the solution of the gold and decompose the cyanide. Compounds of copper are very detrimental. The writer here suggests that weaker ores might in certain cases be treated with very weak solutions of cyanide with the co-operation of an electric current.

Such is the Siemens-Halske process. Here the gold is deposited upon thin sheets of lead. Weak solutions of cyanide, containing about ½ per cent, seem to have a selective action. The gold is dissolved, apparently not as potassium aurocyanide, but as simple auric cyanide. The electric current required is also feeble—a density per square foot of about 0·06 ampère. This process the author considers may prove a serious rival to the McArthur-Forrest process.

The work is written in a thoroughly practical spirit, and will prove invaluable to all interested in gold mining, whether metallurgists or as investors. The eleven plates, mostly drawn to scale, aid greatly in an understanding of the details.

Treatise relative to the Testing of Water-Wheels and Machinery, also of Inventions, Studies, and Experiments, with Suggestions from a Life's Experience. By James Emerson, Mass., U.S.A. Sixth Edition. 1894. 567 pp.

The author of this book, who is evidently on the best terms with himself, is very far from confining himself to water-wheels and turbines, which he understands. He wanders off into the fields of theology, politics, law, mythology, and ethics, subjects quite outside our competence. But he also seeks to belittle science and scientific men, from Newton downwards. He ascribes the telescope, the microscope, &c., to the mechanic! His motto is "The Mechanic to the Front"!—an aspiration for which in these days of strikes there is scant room. He lays down instructions for reaching the North Pole. On this subject one of his reviewers drily observes: "If the world gets in these latest pages of his literary work the best he is capable of rendering it, he cannot do better than set out for that undiscovered country and try his theory as he progresses."

CORRESPONDENCE.

NEW REAGENT FOR SHOWING THE PRESENCE OF HYDROGEN PEROXIDE IN GREEN PLANTS.

To the Editor of the Chemical News.

Sir,—I wish to direct your attention to the paragraph in Chem. News, vol. lxxi., p. 38, referring to A. Bach's "New Reagent for showing the presence of Hydrogen Peroxide in Green Plants."

In its essential features, *i.e.*, the use of aniline as a test, it is not new. I had the pleasure of assisting Dr. Schunck, F.R.S., a few years ago, in an investigation "On the Action of Aniline on Green Leaves and other Parts of Plants." As a result of this action, a definite crystalline substance was obtained, the properties and composition of which were determined. Our observations led us to believe that the brown colouration of the leaves under treatment, and the formation of the crystalline substance, were due to the presence in the leaves of hydrogen peroxide or an active oxidising agent of some kind. The results of the investigation were published in the *Annals of Botany*, vol. vi., July, 1893.—I am, &c.,

Geo. Brebner.

The Jodrell Laboratory, Royal Gardens,
Kew, February 13, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 5, February 4, 1895.

Argon.—M. Berthelot.—This memoir is in substance a reproduction of the communication made to the Royal Society by Lord Rayleigh and Professor Ramsay and already inserted in the Chemical News.

Monoiodoammonidic Derivatives of Hexamethyltriamidotriphenylmethane.—A. Rosenstiehl.—This investigation shows that methyl iodide forms with the complex triamines $A_3\equiv C-\overset{+}{R}$ two series of colourless compounds. The first series contains a single atom of nitrogen entirely saturated. The compounds of this class exchange the radicle $\overset{+}{R}$ with an acid radicle, and are transformed into colouring matters. The second series, formed by the addition of 3 mols. of methyl iodide, contains the atoms of nitrogen entirely saturated. The group $\overset{+}{R}$ in this case is not exchanged for an acid radicle, and does not become coloured.

Laccase, and on the Oxidising Power of this Diastase.—G. Bertrand.—The existence of an oxidising diastase is perfectly extablished by the author's experiments. The intervention of micro-organisms is excluded by the conditions of the process.

Reactions of Chelinodine with Phenols in Sulphuric Solution.—M. Battandier.—At the bottom of a porcelain capsule we place a drop of guaicol and about ½ c.c. of sulphuric acid of sp. gr. 1·84 and mix. At the edges of the capsule we then place some fragments of chelidonine, and cause the acid mixture to touch them, so as to moisten but not carry them away. The capsule being set on a table, we see in a few moments carmine streaks of a remarkable purity and intensity, descending from the fragments of chelidonine towards the bottom of the capsule. This reaction persists for a long time. When it succeeds well, it is one of the most beautiful possible, but it is rather capricious. I have not had the opportunity of trying the pure synthetic guiacol, but with the guaiacol carbonate it is much less intense. This manner of obtaining coloured reactions, which leaves free access for the oxygen of the air, is perhaps susceptible of generalisation. It has already yielded me good results with glaucine. Under the same conditions as guaiacol, thymol gives a rose colouration which lasts for more than twenty-four hours, only becoming slightly purple as the acid becomes hydrated. This reaction always succeeds if the chelidonine is introduced before the sulphuric acid gives a blue colour with the thymol. With ordinary phenol there is only a slight rose tint. Oil of cloves gives a purple, very distinct in spite of the yellowish brown colour which sulphuric acid produces with this oil.

Naphthol α gives streaks of dark green. Naphthol β gives streaks of a brown passing into a violet. Pyrocatechine, roses passing into a violet. Hydroquinone, yellowish streaks. Resorcine also gives yellowish streaks, but soon hidden by the blue colour which this phenol gives with the acid. Phloroglucine gives yellowish streaks passing to a buff. Pyrogallol produces reds, turning to a yellow and slowly disappearing. Gallo-tannic acid gives yellow streaks gradually passing into an intense grass-green. The ethers of the phenols act like the phenols themselves. It is known that chelidonine in a sulphuric solution turns green on the addition of a trace of nitric acid. All oxidising agents produce the same effect. The reaction is especially brilliant with a trace of potassium chlorate in solution or with an arseniate.

Zeitschrift fur Analytische Chemie.
Vol. xxxiii., Part 2.

Detection of Hydrogen Peroxide in Atmospheric Air and in Atmospheric Waters.—Em. Schöne.—The substance of this important memoir, which extends to nearly 50 pages, has been already inserted.

Volumetric Method for the Determination of Phosphoric Acid.—A. F. Holleman.—In the *Recueil des Travaux Chimiques des Pays Bas* (xii., p. 1) the author has communicated a volumetric method for the determination of phosphoric acid which reduces this determination to the titration of silver by the method of Volhard. The principle of the method consists herein, that in the solution of a phosphate, M_2HPO_4, the phosphoric acid is precipitated quantitatively as Ag_3PO_4, if care is taken to remove the nitric acid liberated by the addition of sodium acetate. If, therefore, we use an accurately known excess of a silver solution of known strength, after filtering off the Ag_3PO_4, we may determine (on Volhard's principle) the silver in an aliquot part of the filtrate, and hence deduce the quantity of phosphoric acid. The precipitation and filtration of the silver phosphate must be effected in a dark measuring flask, and a dark funnel, on account of the sensitiveness of this compound to light. If we have to determine the phosphoric acid in the acid solution of a phosphate, or in a solution of a primary phosphate (MH_2PO_4), it is necessary to add to the solution so much of an alkali that phenolphthalein just shows a change of colour. We have then again in solution the salt M_2HPO_4. For the details of this method I may refer to the memoir above cited. Dr. J. J. L. von Ryn has now re-examined this method in my laboratory on a series of solutions of $Ca_3(PO_4)_2$ in nitric acid, containing in 50 c.c. 94·9 up to 190·0 m.grms. P_2O_5, and obtained results given in a subjoined table. The values found agree well with those calculated, only when a large excess of the silver solution was used the phosphoric acid was found rather too high.

On Lard.—Dr. Samuelson.—All the qualitative reactions hitherto recommended for deciding on the purity of lard are not trustworthy, as, in spite of a negative result, a sophistication with a vegetable oil may exist. The iodine number is the main criterion.

Use of Micro-Chemical Reagents in Analytical Chemistry.—W. Lenz.—The "first communication" treats of the determination of ethereal oils, especially in cloves and mace. If possible, the author's methods will be reproduced *in extenso.*

New Execution of the Method of Schlösing for the Determination of Nitric Acid.—Prof. Dr. L. L. de Koninck.—This memoir requires the three accompanying illustrations.

Small Laboratory Apparatus.—Arnold Eiloart.—In this paper we have descriptions and figures of a suspended burette and of a syphon for maintaining a constant level of liquid.

Report on the Progress of Analytical Chemistry.—E. Hintz, with the co-operation of H. Weber.

MEETINGS FOR THE WEEK.

Monday, 25th.—Society of Arts, 4. (Cantor Lectures). "Means for Verifying Ancient Embroideries and Laces," by Alan S. Cole.
— Medical, 8.30.
Tuesday, 26th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Photographic, 8.
— Society of Arts, 8. "Mediæval Embroidery," by Miss May Morris.
Wednesday, 27th.—Society of Arts, 8. "Furnaces for Roasting Gold-bearing Ores," by C. G. Warnford Lock.
— British Astronomical Association, 5.
Thursday, 28th.—Royal, 4 30.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Meteorites," by L. Fletcher, M.A., F.R.S.
Friday, March 1st.—Royal Institution, 9. "The Children's Books of a Hundred Years Ago," by Rev. Canon Ainger, M.A., LL.D.
— Quekett Club, 8.
— Geologists' Association, 8.
Saturday, 2nd.—Royal Institution, 3. "Waves and Vibrations," by Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1840.

HALOGEN ESTIMATION IN ORGANIC COMPOUNDS.

By JAMES WALKER, D.Sc., Ph.D.,
Professor of Chemistry in University College, Dundee,
and JAMES HENDERSON, B.Sc.

Having had recently to perform a considerable number of estimations of the halogen elements in organic compounds by the method of Carius, we investigated the possibility of shortening and simplifying the usual operations by the adoption of a volumetric process. Our experiments have shown that the Carius method can be satisfactorily combined with the Volhard method for estimating silver, whereby a great saving of time and trouble is effected.

A weighed quantity of the substance to be analysed (usually 0·2 to 0·3 grm.) is heated in the ordinary way in a sealed tube with 2 or 3 c.c. of fuming nitric acid and a quantity of solid silver nitrate somewhat in excess of the amount necessary to convert the halogen into corresponding silver salt. The silver nitrate, however, instead of being roughly estimated in the usual way, is weighed off accurately and introduced into the tube preferably in the form of a single crystal. After the oxidation is completed, the tube is opened and the contents washed into a flask with four successive portions of water, the total amount of liquid being 100—150 c.c. The solution, with any precipitate that may have accompanied it, is boiled for ten minutes to expel the lower oxides of nitrogen. It is then cooled, and after the addition of iron alum as indicator, titrated with 0·05-normal solution of ammonium thiocyanate. The amount of thiocyanate required gives the quantity of silver nitrate still in solution, and this, when subtracted from the quantity originally added, gives the amount which has gone to form silver haloide with the halogen present in the organic substance.

In the following example the amount of bromine was estimated both gravimetrically and volumetrically with the same portion, the silver bromide obtained being filtered off and weighed, and the excess of silver nitrate titrated in the filtrate.

0·3458 grm. of substance was heated with nitric acid and 0·4044 grm. of silver nitrate. The amount of silver bromide obtained was 0·3664 grm., and the filtrate required 4·15 c.c. of ammonium thiocyanate solution (1 c.c.=0·01724 grm. $AgNO_3$) for complete precipitation of the silver.

Percentage of bromine estimated gravimetrically .. .. =45·1
Percentage of bromine estimated volumetrically .. .. =45·3

A substance which was found by gravimetrical analysis to contain 33·85 per cent of chlorine gave the following volumetrical results:—

I. 0·3277 grm. substance required 20·0 c.c. of a thiocyanate solution (1 c.c. = 0·00812 grm. $AgNO_3$) after heating with 0·6930 grm. $AgNO_3$, whence Cl = 33·85 per cent.

II. 0·3114 grm. required 14·4 c.c. of the same solution after heating with 0·6183 grm. $AgNO_3$, whence Cl=33·62 per cent.

These results show that the process is sufficiently accurate for ordinary purposes of organic analysis.

The method avoids filtration after the tube is opened, as only the *liquid* contents have to be washed into the receiving flask, it being a matter of indifference whether any of the precipitate remains behind or not. Again, it often occurs on opening a tube that small splinters of glass mix with the precipitate, which necessitates a tedious separation and weighing if the gravimetric method is adopted, whilst the volumetric method is thereby unaffected. If the thiocyanate solution, which should be standardised against a weighed portion of the silver nitrate used in the precipitations, is once prepared, the whole process may be completed in fifteen to twenty minutes after the opening of the tube.

PREPARATION AND PROPERTIES OF TITANIUM.

By HENRI MOISSAN.

Hitherto titanium has been more known in combination than in the free state. It has been previously obtained by Berzelius, Wœhler, Deville, and Kern only in the state of amorphous powders, the appearance and the properties of which varied with each preparation. The strong affinity of titanium for nitrogen, and the difficulty of obtaining a current of hydrogen absolutely free from nitrogen, have greatly complicated the production.

On heating in the electric furnace (100 ampères and 50 volts, 8 horse-power) titanic acid in a crucible, we regularly obtained a titanium oxide, fused or crystalline, of an indigo-blue colour. With a current of 300 to 350 ampères and 70 volts (40 horse-power) we obtain a bronze-yellow mass perfectly fused. This is the titanium nitride of Friedel and Guérin, Ti_2N_2. If we heat in the air in a boat of carbon under the action of an arc of 1200 ampères and 70 volts, the melted mass obtained is titanium carbide, TiC, absolutely free from nitrogen.

For obtaining titanium the author used the rutile of Limoges, carefully selected and containing very little silica and iron, but afterwards substituted titanic acid prepared in the laboratory. It is intimately mixed with carbon, compressed and dried. This mixture was strongly compressed into a crucible of coke of 8 c.m. in diameter, and placed in the middle of an electric furnace. We operated thus upon a quantity of 300 to 400 grms. The arc from a current of 1000 ampères and 60 volts was allowed to play for ten to twelve minutes. The crucible when cold was found to contain a homogeneous mass which had been melted only to a depth of a few c.m. Even with a current of 2200 ampères and 60 volts the fusion was not complete. Beneath the melted titanium was found a layer of yellow nitride, and at the bottom of the crucible a layer of blue titanium oxide. The best specimen obtained (carbide + oxide) yielded 48 per cent carbon and 2·1 per cent of ash. This fused mass may be mixed with titanic acid and, anew, submitted to the action of a current as intense as the former. By this method we obtained a titanium free from nitrogen and silicon, and containing only 2 per cent of carbon.

This titanium forms a mass with fractures of a brilliant white, hard enough to scratch easily steel and rock crystal. Its specific gravity is 4·87.

Chlorine attacks titanium at 325° with incandescence, yielding liquid titanium chloride, $TiCl_4$. Bromine produces at 360° a dark bromide. Iodine reacts at a higher temperature with visible incandescence, forming solid titanium iodide.

Titanium burns in oxygen at 610° with incandescence, leaving a residue of amorphous titanic acid. Sulphur attacks titanium slowly at the softening-point of glass. The sulphide is not attacked in the cold by hydrochloric acid, but with concentrated and boiling acid it gives off hydrogen sulphide.

In a current of nitrogen the powder of titanium forms nitride at a temperature bordering upon 800°. The combination ensues with a liberation of heat. This is the first distinct instance of the combustion of an elementary body in nitrogen. Carbon dissolves in melted titanium, forming a definite carbide. The excess of carbon crystallises out as graphite.

In the electric furnace silicon and boron combine with titanium, forming borides or silicides, melted or crystallised, and having a hardness equal to that of the diamond.

Titanium dissolves easily in melted iron and lead. With copper, tin, and chromium it yields alloys, which are under examination.

Hydrochloric acid, boiling and concentrated, attacks titanium slowly with evolution of hydrogen, producing a violet solution. With hot nitric acid the action is slow, yielding titanic acid. Aqua regia acts more rapidly. Dilute sulphuric acid dissolves titanium much more easily. Hydrogen escapes, and the solution has a violet colour. Titanium is attacked by melting potassium nitrate without apparent liberation of heat; but if titanium in powder is thrown into potassium chlorate heated to its decomposition-point, there ensues a lively incandescence. It is also attacked with incandescence by melting alkaline carbonates, and by a mixture of potassium nitrate and carbonate.

Powdered titanium heated in a current of steam does not decompose the vapour below a temperature near 700°, and the action is not continuous below 800°.

For the analysis of this compound it is melted with a mixture of two parts potassium carbonate and eight parts potassium nitrate. The white mass obtained is taken up in cold water; the insoluble residue is dissolved in cold hydrochloric acid and added to the first solution. The titanic acid is precipitated with ammonia.

The metal yielded:—Titanic acid 96·69, carbon 1·91, ash 0·41.

Titanium nitride forms very hard masses of a bronze colour; it scratches the ruby and cuts the diamond. Its specific gravity is 5·18.

Melted titanium is the most refractory substance which we have as yet obtained with the electric furnace. It is more infusible than vanadium, and goes far beyond pure chromium, tungsten, molybdenum, and zirconium. Melted titanium has a less affinity for nitrogen than the powders obtained by the action of the alkaline metals upon the fluotitanates. Still, this titanium, if reduced to powder, burns in nitrogen at a temperature of 800°.

In the totality of its properties, titanium distinctly approaches the non-metals, especially silicon.—*Comptes Rendus*, cxx., p. 290.

ON CERTAIN PERCEPTIBLE REACTIONS OF THE AMIDO-BENZOIC ACIDS.

By OECHSNER DE CONINCK.

These reactions have been employed by the author in analysing mixtures of amido- and nitro-benzoic acids.

He makes known the behaviour of the alkaline hypochlorites, hypobromites, and hypoiodites, of calcium hypochlorite, and of ferric chloride, in very dilute aqueous solutions.

I. *Action of Alkaline Sodium Hypochlorite on the Amido and Nitro-Benzoic Acids.*

With the ortho-amido acid the liquid turns to a blood-red. With the meta-acid, a red-brown. With the para-acid, an orange-red.

The three nitro-acids give no result under the same conditions.

II. *Action of Alkaline Sodium Hypobromite on the same Acids.*

With the ortho-amido acid the liquid takes a deep orange-red. With the meta- and para-acids, a bright orange-red.

The three nitro-benzoic acids give no result.

III. *Action of an Alkaline Sodium Hypoiodite.*

The author prepares the reagent by dissolving, in an excess of pure concentrated soda-lye, a little iodine until a yellow colour begins to appear.

With ortho-amido benzoic acid the liquid turns to an orange-red. With the meta-acid, a dull yellow. With the para-acid, a decided yellow. With the nitro-acids, nothing similar; the crystals of the ortho-isomer become deep yellow in contact with the reagent, but the liquids are not coloured as in the other reactions.

IV. *Action of Alkaline Potassium Hypochlorite.*

With the ortho-amido acid, a very deep red-brown. With the meta-acid, a dark red-brown. With the para-acid, a dark orange-red.

No coloured reaction with the nitro-benzoic acids.

V. *Action of Alkaline Potassium Hypobromite.*

With the ortho-amido benzoic acid the liquid takes a bright orange-red. With the meta- and para-acid, the same tint.

No result with the nitro-benzoic acids.

VI. *Action of the Alkaline Potassium Hypoiodite.*

This reagent has been prepared like the sodium hypoiodite. With the ortho-acid, a red-brown liquid. With the meta-acid, a deep orange. With the para-acid, a bright orange. With the nitro-benzoic acid, no colour.

VII. *Action of Alkaline Calcium Hypochlorate.* (*Dilute Solution.*)

With the ortho-acid, a deep violet colour, soon turning to black or to dirty green. This reaction is very sensitive. With the meta- and para-acids, a yellow-brown.

No reaction with the nitric acids.

VIII. *Action of Ferric Chloride in a very Dilute Watery Solution.*

With the ortho-acid, a rose-colour, turning to a wine-red. With the meta-acid, amber-yellow. With the para-acid, a red-brown.

No reaction with the benzoic acids, though the crystals of the ortho-isomer after a time take a light red colour.—*Comptes Rendus*, cxx., p. 100.

THE SEPARATION OF ARSENIC, TIN, OR ANTIMONY, FROM LEAD, COPPER, SILVER, CADMIUM, COBALT, NICKEL, &c.

(A Preliminary Communication).

By P. JANNASCH.

Some time ago I made known, in the *Zeitschrift fur Anorgan. Chemie*, a method for the quantitative determination of arsenic in sulphides (after previous oxidation) by a final heating in a current of dry hydrochloric acid vapour, and I described the apparatus in full.

For some time, in concert with F. Schmitt, I have been engaged with extending the dry hydrochloric acid process in general to the separation of arsenic from a series of other metals, and with the very best results. We used for our quantitative separations of arsenic an air-bath of nickel, capable of being closed and fitted with thermometers and windows of mica, in which my glass apparatus (formerly described) can be heated to given temperatures up to 450°. The metals to be separated, or their compounds, are dissolved in the glass apparatus with nitric acid or aqua regia, &c., dried therein, and then distilled at the required temperature in a current of hydrochloric acid gas. The arsenic, collected in especial receivers, is then separated and weighed. In a separation of arsenic and tin, attempted in this manner, we observed the great solubility of the tin chloride present, and have thereupon set about the direct separations of this metal from less volatile metals, such as lead, copper, &c. Here the tin also is collected in especial receivers, subsequently precipitated from the solutions as tin sulphide by means of ammonia, and ammonium sulphide with acidulation, and finely weighed as tin oxide.

The statement of Drown and Eldridge (last issue of the *Zeit. Anal. Chemie*) on the volatility of tin chloride has induced me to make this preliminary communication in order to secure the continuation of our work on the lines we have hitherto taken for the direct separation of tin from the less volatile metallic chlorides. Drown and Eldridge have already effected the indirect separation of lead and tin by the repeated evaporation of their chlorides, and we have already obtained the same separation in a direct manner by volatilising the tin in a dry current of hydrochloric acid at 200°, collecting the distillate of stannic chloride in receivers containing water acidified with hydrochloric acid. We reserve full accounts of our separations of arsenic, tin, and antimony, from the less volatile metals, and analogous experiments in a current of dry hydrobromic acid gas.

EXCLUSION OF SULPHURETTED HYDROGEN IN QUALITATIVE ANALYSIS: ITS REPLACEMENT BY THIOACETIC ACID.

By ROB. SCHIFF and N. TARUGI.

If to a hydrochloric solution of the metals of the second group we add a faintly ammoniacal solution of ammonium thioacetate, and heat to near the boiling-point, the metals are at once deposited as sulphides, and the odour of sulphuretted hydrogen given off is very slight. After cooling and filtration there is found in the filtrate no trace of metals, even if arseniates were originally present, the complete precipitation of which by present methods is well known as exceedingly difficult.

The mixed sulphides are separated by the ordinary methods, and the filtrate—after being boiled for a few minutes—is used for the recognition of the next following groups. From ½ to 1 grm. of material are taken for analysis, and for such quantities 1·5 to 2 c.c. of a 30 per cent solution of ammonium thioacetate is in general sufficient for a thorough precipitation. Sulphur is never deposited during the reaction, and no disturbing products are introduced in the operation. The reagent—

$$CH_3.C:O(S.NH_4)$$

is easily obtained by the action of glacial acetic acid upon phosphorus pentasulphide; it boils at 95°, has an unpleasant odour, and is sparingly soluble in water. If the acid is dissolved in a slight excess of dilute ammonia, we obtain a yellowish liquid of a faint odour, resembling that of ammonium sulphide. It is diluted to three times the volume of the original acid. It is served out to the students in small bottles, through the cork of each of which is thrust a pipette holding about 2 c.c.

Arsenites and arseniates give in the cold a whitish turbidity, but in heat an immediate and complete precipitation of arsenic trisulphide.

Bismuth, copper, and stannic and stannous salts are partially precipitated in the cold, but completely in heat.

Lead salts, in the cold, a dark red precipitate, which if heated changes to lead sulphide.

Silver salts.—Silver chloride, dissolved in hot concentrated hydrochloric acid, is completely precipitated as silver sulphide. Silver chloride, bromide, and iodide, if heated with a solution of thioacetate, are completely converted into silver sulphide.

Cadmium salts.—The sulphide is known to be moderately soluble in hot hydrochloric acid. Whilst being heated with the reagent in a hydrochloric solution the precipitate sometimes dissolves, but it is re-deposited when cold.

Mercuric salts.—In the cold a red precipitate (sulphochloride); in heat, conversion into black sulphide.

Platinum salts.—Cold, a red precipitate; in heat, a complete conversion into platinum sulphide.

Gold salts.—Exactly like platinum.

Ferric salts.—Instantly reduced to ferrous salts.

Chromic salts.—Instantly reduced to chrome salts.

Aluminium, manganese, nickel, cobalt, zinc, &c.—Salts in acid solution are not affected.

The nickel, cobalt, and zinc, &c., sulphides in ammoniacal solutions, are at once thrown down. But we see no reason for substituting ammonium thioacetate in separating metals of the fourth group.—*Berichte*, vol. xxvii., p. 3437.

CRUCIBLE TOOL-STEEL.

By SERGIUS KERN, M.E., St. Petersburg.

In the summer of last year, we constructed at the New Admiralty, St. Petersburg, a coke furnace for melting crucible steel. Into the furnace four crucibles are placed, which contain each a charge of 80 pounds. The daily output is eight poods of crucible tool-steel, or soft steel for castings, as besides preparing tool-steel ingots (4 inches × 4 inches) we introduced the manufacture of steel castings, weighing up to 5—6 poods (1 pood = 36·11 English pounds).

This Government establishment, the New Admiralty, has three ship-building yards; out of them, two are substantial brick structures, and the third is wooden. The climate here commands closed yards. For the working of mild sreel in the construction of war-ships, nearly exclusively foreign tool-steel was used. The necessary steel castings, if wanted, were ordered at the steel-works situated in St. Petersburg.

We constructed the steel-melting furnace in the iron-foundry of the Admiralty, using the existing chimney for the boiler and copper-melting furnaces. Want of space and other reasons induced us to alter the ordinary adopted dimensions. The soft iron for the melting and the crucibles were supplied by the Obouchoff Steel Works. The works prepare this iron from the steel turnings of their mechanical shops, where ordnance is manufactured; the iron is very clean.

Carbon	0·12 per cent
Manganese	0·07 ,,
Silicon	0·11 ,,
Sulphur	0·01 ,,
Phosphorus	0·02 ,,

For the manufacture of tool-steel we melt this iron with a certain amount of refined Swedish pig-iron. When melting for steel castings, the charge consists of iron mixed with puddled steel or scrap in the form of rounds, received during the punching of holes in ship plates. The latter is a cheap and good substitute for puddled steel. The steel castings have the following composition:—

Carbon	0·47 per cent
Manganese	0·33 ,,
Silicon	0·14 ,,

The castings are all annealed, and in this case we find that steel of this chemical composition is specially suitable.

We use ferro-aluminium for small castings, but for castings of more than 3 poods prefer silico-spiegel (10 per cent of silicon, 14 per cent of manganese). In heavy castings, weighing several tons, the use of ferro-aluminium is nothing more than waste of money.

The tool-steel ingots, weighing two poods each, are hammered into sizes in the forge of the Admiralty. If thus the tool steel is manufactured on a small scale by the shipyard itself, we must conclude that this operation will be always a remunerable business, especially when at intervals of this line of work small steel castings are made which are often wanted in ship-building.

THE ABEL TEST.

By J. H. B. JENKINS.

In the accompanying diagrams the rate of heating of a burning petroleum oil in the Abel flash-point apparatus is shown. In Fig. 1, the usual conditions are represented; the temperature of the water-jacket falling from 130° F., whilst the oil's temperature is raised from 60° F. In Fig. 2, the initial temperature of the water-jacket is 180° F., whilst the oil starts on one occasion from 60° F., and on another from 90° F.

From Fig. 1 we see that just after the start the rate of heating of the oil approximates to 3 degrees per minute. Twenty minutes later, the rate of heating is only one-fourth as great, and the temperature of the oil is about 90° F. An hour after the start, the oil reaches its maximum of about 99° F., and after remaining for many minutes, it slowly falls again.

A consideration of the design of the instrument shows that many likely sources of error in flash-point determinations are obviated by it, though its applicability has been consequently narrowed. The apparatus, used without modification, is only applicable to oils flashing below, say, 90° F., and even up to that temperature the rate of heating is about four times as great at first as it is at last,

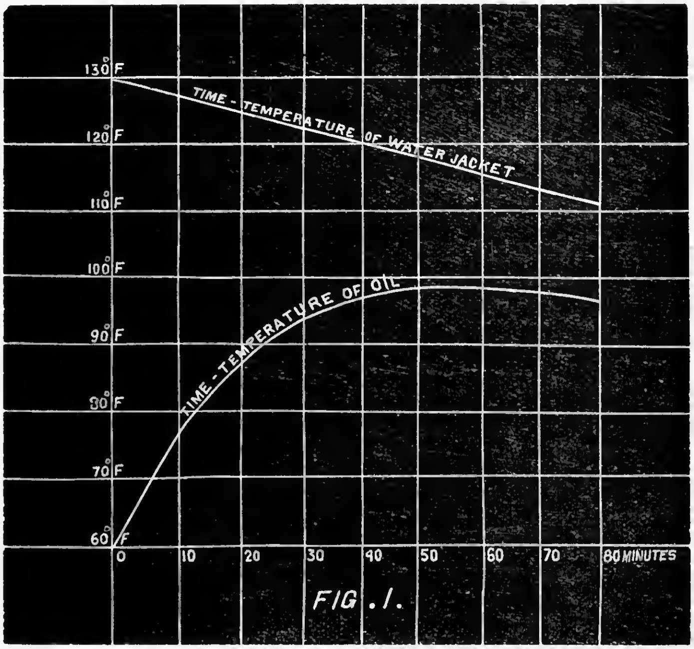

FIG. 1.

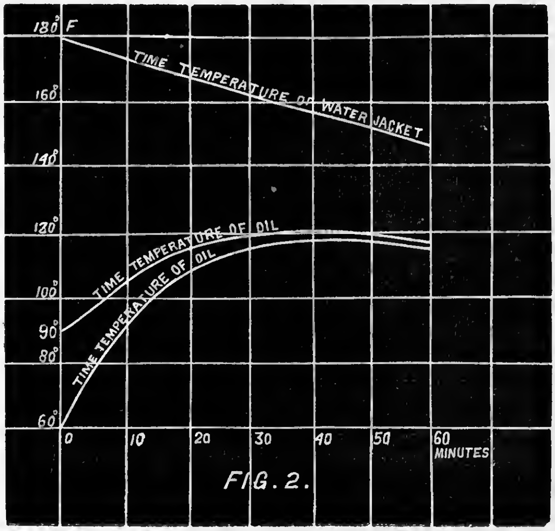

FIG. 2.

What is wanted is an apparatus in which the oil would be heated regularly, and which would serve, without modification, to test all burning oils up to 130° F. or 150° F. flash-point.

It might be well if some such body as the Society of Public Analysts or the Society of Chemical Industry were to express an opinion as to the highest flash-point which should be taken by the Abel apparatus used without modification, and then exactly in what way the conditions of testing should be altered. This would lead to more uniform results for high flash-points.

Are the instruments standardised by the Board of Trade with a pendulum 24 inches long or only 13 inches long, such as they are issued with? Is there no way of preventing the pendulum mistake being repeated?

The suggestion has been made of a stirring arrangement to mix up the oil vapour and air in the cup, but the advantage would scarcely compensate for the extra complication of the apparatus, and may prove a fresh source of error. It cannot be insisted that the Abel test will detect quite the lowest temperature at which the vapour of an oil may be flashed under any possible conditions; but if oils of identical inflammability give the same flash-point by the apparatus, and the flash-point given is always proportional to the inflammability, it is better to retain the present simplicity of the instrument, rather than aim to get results a degree or two lower by less certain methods.

Sometimes the flash-point of an oil obtained from different instruments may be reported as varying a few degrees; this may be partly dependent upon an earlier partial flash, which sometimes escapes notice, but which leaves in the vapour-space sufficient combustion products to delay the next flash for two or three degrees.

G.E.R. Laboratory, Stratford, E.,
February 13, 1895.

THE SECRET OF THE BROWNIAN MOVEMENTS.*

By R. MEADE BACHE.

(Concluded from p. 97).

FIXED oils have not the same molecular constitution as volatile oils, nor these the same as alcohol, nor either the same as water. Whatever these differences may signify in various behaviours under varying conditions, one, among the rest, distinguishes water from the rest and all other liquids. Despite its apparent perfect fluidity, the reluctance of its molecules to move among themselves as smoothly as do those of other liquids among themselves is one of its most evident characteristics. We see this exemplified by the way, long since ably demonstrated, in which a wave is built up from ripples, by the way in which the surf breaks along the shore, and in the ease with which a small proportion of oil in contact with water modifies or subdues its energy. Only recently I steered a boat in Boston harbour between two headlands, between which, and far beyond, white-caps covered the surface of the water, surrounding a placid lakelet of a square mile in area, black by contrast to its white-capped margin, over the surface of which lakelet I was soon smoothly gliding; and this change from turbulent to placid waters was wholly due to the merest film of oil from Boston's great sewer discharging its contents three miles away on the lowering tide from the head-house on Moon Island into the current running towards the sea. I am aware, of course, that part of the calmness described was owing to the fact that the oil lessened the friction of the wind on the water. But that was not the only cause of the calming effect produced by the oil. Oil prevents the friction of parts on the surface of water already in agitation, and thereby quiets the wave already risen. The area which I have just described as a smooth lakelet had been only a short time before my arrival at the place in precisely the same state of agitation as the surrounding waters. The surface is the part where the wave begins to form, and where it receives constant increments, the wind propagating these, and by impact on the growing wave or billow as a whole, forming and propelling it as a mass, despite its tendency in deep water to oscillate freely in the vertical without translation horizontally. It is easily conceivable that, although particles of oil may, as I have stated, experience no sensible friction when in contact with the molecular movements of water, so almost infinitesimal are they in range, yet that oil forming a film over a large surface of water may, through friction, as an enclosing sheath, tend to quiet the water, and thus impair and gradually destroy its ability to continue the massed effect known as a wave, at the place, the surface, where not only is it generated, but where it most effectively tends to preserve its energy of movement.

Thus, it is not only through its weight that water, when set in active motion, becomes so formidable as we know it to be when in angry mood. It is because, besides the momentum with which it can be endowed through its great weight, it lends itself, through its molecular constitution, to the storage of enormous energy and to the yielding up of that energy reluctantly. Assuming the existence of a sea of oil or one of alcohol, and either in a state of turbulence, and moreover eliminating in imagination the difference in weight between these and water, either in comparison with water equally turbulent would gently come to rest.

The difference between Herr Wiener's view and mine is radical. He speaks of the motion common to fluids as the cause of the brownian movements. But such motion, at least as perceptible through the microscope, does not exist, except in water or in some other liquid in which water is, as I have proved by experiment, a considerable constituent. Then Herr Wiener, although accounting for the brownian movements by hypothetical movements common to all fluids, really makes their causation the vibratory effect of rays of light and heat, to which, he thinks, fluids through their constitution lend themselves. I, on the contrary, show that the molecular motion, called brownian, taking place under all conditions imposable, is a property of water and of water only, and that light and heat have naught to do with producing it, although, as I have admitted, they may possibly act in intensifying it. All that I may claim to have detected is a phenomenon which reverts to the molecular constitution of water, as to which the moving solid particles in it concerned in the brownian movement have no more to do than has a current-metre to do with the flow of the stream the swiftness of which it measures. We do not deny that a gas may be essentially pure, and therefore homogeneous, a chemical as well as physical entity, and that, nevertheless, its molecules may have repulsions among themselves: on the contrary, we affirm it. Similarly water, recognised, as it is, as a chemical condition, not a mechanical mixture, has, as here demonstrated, repulsions among its molecules.

When I take into account all that I have detailed, and remember also that these moving particles of which we have been speaking, hermetically sealed under glass, as I have them now under cover-glasses, move indefinitely in time, unmodified in range and velocity, through changes of temperature, through light and darkness, through electricity and magnetism, in the presence of every force to which I have been able to subject them, I cannot but think, when I add that these movements are active in proportion to the fineness of sub-division of the particles, that they are caused by the mutual repulsions of the molecules of aqueous fluids. Did I see a relatively large mass moving as vigorously as the most minute one visible

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* Read before the American Philosophical Society, April 20, 1894, —From the *Proceedings of the American Philosophical Society*. xxxiii., No. 145.

to the eye, I should regard this theory as untenable from that single fact alone, because it would be impossible that molecular action should concentrate effect on a relatively great mass; but when I see, as I do, the largest masses remaining unmoved, and descending in the scale, smaller ones, showing the effects of a faint impulse, and descending further still, others exhibiting sluggish movement, until the sight reaches the smallest particle visible, finding in that the most eccentric and vehement movement of any exhibited, I know then that I am looking at a sea where the little waves dash in vain on the impressionless rocks, barely disturb the floating ships and hulks, but twist and swirl and make frantically dance the little cockle-shells of boats wherever they may happen to be upon the surface; and that, in fine, I am witnessing the molecular movement of this sea in its effort to escape into space. The aqueous fluids, finding no release, as under my cover-glasses, the movements would go on for ever; finding it in freedom from confinement, they go on until the fluid which is the condition of their manifestation is in a few minutes dissipated in evaporation.

I must confess that, although every conclusion reached through labour bestowed gives a certain pleasure in legitimate appetite for knowledge gratified, yet this is so far beneath what I had thought might lie hidden under the mystery of the brownian movements, I experience a sense of disappointment. I had thought that this investigation might be one of the paths that lead to the solution of the question whether or not energy is immanent in matter or a thing apart from it. For many years after the beginning of this century nothing fundamental in physics was known beyond the fact that matter is indestructible. It has been learned since, but no longer ago than about fifty years, that energy also is indestructible. It still remains, perhaps, to be shown that energy is but an emanation and manifestation of matter reacting on it. Advanced as our knowledge is within a few years as to molecular movement, I had hoped that the investigation of the brownian movements might yield some contribution to molecular theory, and thence lead to a profounder knowledge than we now possess of molecular behaviour in the abstract. I am able, however, to claim for the demonstration here no more than that the brownian movements are not the self-movements of finely divided particles in suspension in aqueous solutions, which Herr Wiener had also ascertained, but simply that which he did not ascertain, movements generated by the molecular action of aqueous fluids, instead of being, as he and Herr Exner also thought, in differing form, phenomena due to light and heat. Perhaps even this moderate conclusion may be disputed, but it remains to be disproved.

Determination of Fat in Cheese.—Stefan Bondzynski.—The author's method consists in introducing a measured quantity of milk into a suitable tube, mixing the milk with concentrated hydrochloric acid, and heating until the precipitated casein is re-dissolved. Ether is then added, and the fat is determined in a known volume of the ethereal solution. This method is applicable to the determination of the fat in cheese. A portion of the cheese is ground up to a fine paste, and a weighed quantity is introduced into a tube, and mixed with 20 c.c. of hydrochloric acid of sp. gr. 1·1. On cautiously heating upon a wire netting, the cheese dissolves and the fat collects in a fused state on the surface. The tube is cooled, and about 30 c.c., of ether added. The fat dissolves quickly when the contents of the tube are allowed to stand at a temperature of about 40°, when the strata of acid and of ether-fat separate sharply from each other. The volume of the ether-fat solution is read off, 20 c.c. are drawn off with a pipette and introduced into a tared Erlenmeyer flask; the quantity is determined, and calculated for the entire ethereal solution.—*Zeit. f. Anal. Chemie.* xxxiii., Part 2.

A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF NITROUS OXIDE.

By GEO. T. KEMP.

(Preliminary Communication).

The necessity for further research on the methods for the quantitative determination of nitrous oxide is readily seen from a brief review of the past work on the subject. The method most frequently employed is that recommended by Bunsen,[*] which consists in exploding with hydrogen, by which the nitrous oxide is reduced to water and nitrogen according to the equation—

$$N_2O+H_2=N_2+H_2O.$$

The shrinkage in volume after the explosion is equal to the original volume of nitrous oxide present. This method has not met with general favour, as several observers have found the reaction not to be a clean one, side reactions giving rise to oxidation or reduction products, according to different conditions varying with the ratio of hydrogen to nitrous oxide and with pressure.

Frankland[†] refused to report positively on the question as to whether nitrous oxide was decomposed in the human body during anæsthesia, as he had no satisfactory method of determining the nitrous oxide in the inhaled and exhaled air. He says, "The separation of nitrogen and nitrous oxide presented quite unlooked-for obstacles, since their explosion with excess of hydrogen, instead of liberating free nitrogen from the nitrous oxide as commonly supposed, gives rise to the formation of nitrous acid and ammonia likewise." Using a large excess of hydrogen, and exploding under reduced pressure, gave better results, but "not so sharp as he could wish."[‡]

Practically the same side reactions have been encountered by Goltstein, Winkler, and Lunge. Goltstein[§] speaks of the method as "Höchst ungenau." Lunge[‖] says that with hydrogen or oxyhydrogen side reactions, which render the results useless, readily take place.[¶] Winkler[**] hoped to avoid the side reactions mentioned above by passing the gases over palladium asbestos; but though the decomposition into nitrogen and water took place readily, the results were not constant. A white cloud of ammonium nitrate or nitrite was sometimes seen. The method has been advocated by Dummreicher and by Hempel. Dummreicher,[††] apparently, was not acquainted with the adverse criticisms on the method, for he says that Bunsen's work was the only one with which he was familiar. He found that the method gave satisfactory results, and spoke of the reaction as smooth (glatt).

Hempel[‡‡] also advocates explosion with hydrogen. Replying to Lunge's[‖‖] article, which called attention to side reactions, he makes no criticism beyond saying that these were likely due to impurities in the gas. The purest gas which Hempel obtained from ammonium nitrate was 98 per cent N_2O, and 2 per cent N. He exploded this gas with hydrogen, in varying proportions alone, and with the admixture of oxyhydrogen gas. He finds the best mixture of hydrogen and nitrous oxide to be when—

$$N_2O : H :: 1 : 2 \text{ or } 3.$$

When oxyhydrogen gas is added it should be in such proportion that, independent of the amount of nitrous oxide and hydrogen, there shall be 26 to 64 volumes of oxyhydrogen gas to every 100 volumes of non-explosive

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[*] Bunsen, "Gasometrische Methoden," 1878, p. 60.

[†] *Transactions of Odontological Society, Great Britain*, 1872-73.

[‡] *Op. cit*, p. 20.

[§] Goltstein, *Arch. f. d. gesammt. Physiologie*, 1878, p. 338.

[‖] Lunge, *Berichte*, xiv., p. 2190.

[¶] "Bei der Verbrennung mit Wasserstoff oder Knallgas treten dann leicht unangenehme Nebenreactionem ein welche die Resultate unbrauchbar machen."

[**] Winkler, "Industrie Gaze," ii., 1877, p. 427.

[††] Dummreicher, *Monatsheft für Chemie*, 1881, i., p. 732.

[‡‡] Hempel, *Berichte*, 1882, xv., p. 903.

[‖‖] Lunge, *loc. cit.*

gas.* He exploded with hydrogen when the ratio of H to N_2O was as low as 1·6 : 1, in which experiment the explosion was so violent as to break the apparatus, but he does not mention any side reactions. When—

$$N_2O : H :: 1 : 4·6,$$

he found the mixture to be no longer explosive. He makes no mention of having tested his residual gas for ammonia after any of his explosions.

It may be of interest to add that Bunsen himself speaks of this, his method, as not being entirely satisfactory, but he does not speak of side reactions. In his "Gasometrische Methoden" he only gives one experiment, and, as far as I can find, this is all he made.

Several other methods for determining nitrous oxide have been suggested, but none are without objection; and a careful review of the literature has shown that only one of these methods has advocates besides the author who proposed it. This method is one proposed (for nitrous oxide) by Lunge,† and consists in absorbing the nitrous oxide by a considerable quantity of absolute alcohol, and allowing for the amount of other gases absorbed. Alcohol has a high coefficient of absorption for nitrous oxide in comparison to other gases. Lunge says the results by this method are always too high. For example, from a mixture containing 53·1 per cent of N_2O, he obtained 54·7 per cent. This method was used by Goltstein,‡ who found it superior to exploding with hydrogen, and, on the whole, satisfactory.

After finding that ammonia was formed in the reaction of nitrous oxide with hydrogen in the presence of an excess of hydrogen over platinum or palladium asbestos, Winkler§ suggests that a large excess of hydrogen be added, and that the gas be subjected for some time to the action of weakly heated platinum or palladium asbestos, claiming that the nitrogen of the nitrous oxide is, for the most part (der Hauptsache), transformed into ammonia. The ammonia is then determined by standard acid. He recommends this method in cases where the amount of nitrous oxide is very small.

Lunge‖ has tried this method, and criticises it severely. He finds that a comparatively small amount of the nitrous oxide is converted into ammonia. Another method suggested by Winkler¶ is to pass nitrous oxide over a glowing palladium wire in a tube or in a grisoumeter. The nitrous oxide is split up according to the following reaction:—

$$\underset{2\text{ vols.}}{2N_2O} = \underset{3\text{ vols.}}{2N_2 + O_2},$$

so that the amount of nitrous oxide present is equal to twice the increase in volume. Winkler says of this method that it is the only one which has given really satisfactory results. Lunge has tried this, but says it is not quantitative. Moreover, the decomposition is not a clean one, as various oxides of nitrogen are formed and the mercury is attacked. The presence of nitrogen peroxide, NO_2, was shown by the gas becoming brown.

The author of the present paper was led into the investigation, of which it is an account, by being confronted, in some pharmacological work on anæsthesia by nitrous oxide, with the problem of determining nitrous oxide in the presence of nitrogen, the total amount of gas being only 4 or 5 c.c., and the nitrous oxide an unknown part of this, but likely as much as 80 or 90 per cent, thus leaving an exceedingly small residue of nitrogen.

Both Bunsen's method of exploding with hydrogen, and Winkler's method of decomposing the nitrous oxide over a hot palladium** wire were tried, but the results obtained were decidedly unsatisfactory. In working with nitrous oxide all the manipulation of the gas must be carried on over mercury, as water absorbs a considerable amount of the gas. In decomposing nitrous oxide with a glowing platinum wire, in a grisoumeter over mercury, the author's results were similar to those obtained by Lunge, viz., the gas became brown, showing the presence of nitrogen peroxide, NO_2, and though it might clear up, showing a possible decomposition of the NO_2 into nitrogen and oxygen, there was always a thick brown layer where the surface of the mercury had been attacked, thus binding the oxygen in a way which makes the method useless.

After a large number of determinations by exploding with hydrogen, I was forced to agree unequivocally with previous observers who found the method inaccurate because of side reactions. This could not be due to impurities in the nitrous oxide, for that was prepared by the method suggested by Dummreicher* of surrounding the retort, in which the ammonium nitrate is heated by a bath of molten metal of low fusing-point. By taking this precaution to obtain uniform heating of the fused ammonium nitrate, and selecting clean well-formed crystals, the fused mass remained clear as water and the decomposition was a clean one, yielding N_2O about 100 per cent pure, as shown by the analyses by the carbon monoxide method, which will be described later.

After exploding nitrous oxide with hydrogen in the Bunsen eudiometer in such proportions as to form an explosive mixture, and finding the results unsatisfactory, I was informed by Prof. Orndorff, of Cornell University, of some unpublished experiments of Mr. B. S. Cushman, in the Cornell laboratory, in which he found that mixture of gases no longer explosive (*e.g.*, oxygen and a large excess of hydrogen) could be smoothly burned out over a glowing platinum wire in a grisoumeter, the results being, if anything, more satisfactory than by explosion. Hoping that by avoiding the violent reaction of explosions, and using a larger amount of hydrogen, I might escape the side reactions, I made a series of combustions in the grisoumeter, and at first felt encouraged, for there was no evidence of the formation of the oxides of nitrogen or their acids in the presence of the large excess of hydrogen, and the mercury was not attacked.† The results were discordant, however, some coming out exactly, and some varying widely from 100 per cent and from each other. In all experiments but one the reading was exact, or there was too much contraction after combustion. This persisted after extra precautions were taken to prevent the possible escape of hydrogen. The only explanation that suggested itself was the formation of ammonia, which, so far as I know, has never been tested for in such experiments. The test was made, after combustion, by bubbling the gas through ammonia-free water, in a Varentrap bulb, and treating this water with Nessler's solution. The results varied from a negative test to a deep yellow colour, showing the formation of ammonia in varying amounts in the different experiments, which proves the method to be untrustworthy. Washing out the grisoumeter and testing the wash-water gives a better result than bubbling the residual gas through water and testing that. It seems that most of the ammonia is absorbed by the water formed in the reaction, which condenses on the surface of the mercury and on the glass. I was not able to find any factor that governed the formation of ammonia, unless it was true that the hotter the wire the greater was the tendency for its formation. Within the limit of the few seconds or minutes required for combustion, the time did not appear to have any effect. The addition of oxyhydrogen gas did not prevent the formation of ammonia. Two such experiments were made, in both of which ammonia was formed. The ratio of oxyhydrogen gas to the excess of hydrogen beyond that needed to unite with the oxygen of the nitrous oxide was as 8 to 100 in one case, and as 15 to 100 in the other. The explosions were quite violent, and I feared to add as

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* *Op. cit.*, p. 910.

† Lunge, *op. cit.*, p. 2191.

‡ *Arch. f. d. gesammt. Physiologie*, 1878, p. 337.

§ *Op. cit.*, p. 429.

‖ Lunge, *Berichte*, xiv., p. 2191.

¶ Winkler, "Industrie Gaze," ii., 1877, p. 260 and p. 426.

** In the author's experiments only platinum wire was used.

* *Monatsheft f. Chemie*, 1880, i., pp. 735, 741, and 742.

† In a few experiments an exception is noted, but always as doubtful and trifling in amount.

much as Hempel recommended* (26·64 to 100), lest by breakage of the apparatus I should bring the work to a temporary standstill. These experiments differ from Hempel's, also, in being made in the grisoumeter over a glowing platinum spiral instead of with the spark, so that they are not in every respect comparable.

Since hydrogen gave such little promise of success, I tried various methods for reducing the nitrous oxide with carbon. The first method employed was to pass a series of electric sparks between specially constructed carbon electrodes. This decomposed the gas more rapidly than it reduced it. Carbon monoxide and carbon dioxide were formed, but oxides of nitrogen were formed at the same time. The mixture became brown and the mercury was attacked. The next method yielded better results. A piece of gas carbon was filed into a small cylinder about as thick as a match stick and about 6 m.m. long. A platinum spiral was coiled around this, and the whole introduced into the grisoumeter. Upon closing the circuit the spiral glowed and heated the carbon. In an atmosphere of nitrous oxide the carbon burned with great intensity, and reduced the nitrous oxide to CO and CO_2. Thinking that cyanogen might be formed in this reaction, as ammonia had been with hydrogen, I tested the residual gas in several experiments, but not a trace of cyanogen was found. I hoped by continuing the combustion to get all the gaseous carbon in the form of carbon monoxide, which would have doubled the volume of gas after combustion and halved the error of reading, thus—

$$\underset{\text{1 vol.}}{N_2O} + C = \underset{\text{2 vols.}}{N_2 + CO}.$$

This I found to be impossible, however, for even at the and of an hour's combustion there was a considerable amount of carbon dioxide present. To have determined the amount of nitrous oxide originally present, from the carbon monoxide and carbon dioxide formed in its reduction, would not have been as convenient as the next method tried, which proved to be both convenient and accurate. This method consisted in burning the nitrous oxide with a considerable excess of carbon monoxide in a grisoumeter, and determining the CO_2 formed, from which the nitrous oxide could be calculated. Before I had taken up the grisoumeter work on hydrogen, Prof. Morse suggested to try explosion with carbon monoxide. While working with Bunsen eudiometers I tried this, but found the results unsatisfactory. With a small excess of carbon monoxide the explosion was violent; with a large excess the mixture would not explode, and in no case was the nitrous oxide completely reduced. Somewhat better, though not satisfactory, results were obtained by explosion in the grisoumeter later. Whether the difference is due to the different pressures in the two forms of apparatus I am unable to say, but it appears the most likely explanation. My own results in the experiments on nitrous oxide and hydrogen in the grisoumeter were quite in accord with the more extended observations of Cushman, already referred to, as to the ease and completeness with which non-explosive mixtures may be burned out over a glowing platinum spiral; so I determined to apply this method to the mixture of nitrous oxide and carbon monoxide, which had not yielded satisfactory results on explosion.

The grisoumeter usually employed for combustions over water† is not suitable for use with mercury, so that a proper form was improvised by using an ordinary Hempel pipette for solid reagents. To fit into the neck of this is chosen a rubber stopper with one hole. Through this hole is passed a piece of glass tubing, open at each end, but drawn out so as to form a shallow neck about 10 m.m. from the end which extends into the grisoumeter. The lower end (below the stopper) is bent into a gentle curve, or an obtuse angle, for convenience of connection with a rubber tube. Into this glass tube, at any convenient point below the stopper, a piece of platinum wire is fused. The platinum spiral is made of fine wire, which is twisted, at each end, on to a piece of heavier platinum wire, so thick as not to be much heated by a current which will glow the spiral. The piece of stout wire connected with one end of the spiral is passed into the open end of the glass tube; the piece at the other end of the spiral is twisted two or three times around the constriction in the tube, for firmness, and the end then allowed to hang down beside the tube. The wire should be of sufficient length to reach to at least 40 m.m. below the top of the tube, after having passed twice around the constricted neck. The spiral can now be fixed in any convenient position above the top of the tube by bending the stout wire. Connected with the lower end of the glass tube outside the grisoumeter is a piece of rubber tubing somewhat longer than the grisoumeter is high. To the free end of this is attached a funnel, by which the rubber and glass tube may be filled to the top with mercury. When so filled the rubber tube is closed, by a stout pinchcock, close to its connection with the glass tube, The funnel is supported by a separate stand. The platinum wire fused into the glass tube below the cork is thus connected, with the spiral, by the column of mercury in the tube, and, when the mercury stands high enough in the grisoumeter to touch the platinum wire on the outside of the tube, the circuit can be closed through the spiral by connecting one pole of a battery with the platinum wire fused into the glass tube, while the other pole is connected with the mass of mercury filling the grisoumeter. This is best done by an iron wire passed straight down through the small bulb of the grisoumeter until it strikes the mercury.

The results of my experiments with this method are given in the following table. It must be borne in mind that the readings were all made in Hempel's burettes for technical gas analysis, and that these were not specially calibrated, so that the probable error is about ±0·1 c.c.

Experiment.	Taken c.c.	Found c.c.	Ratio. $CO : N_2O$.
August 28, Burette 3 ..	9·8	9·8±0·1	5·0 : 1
,, 28, ,, 2 ..	9·7	9·7 ,,	6·4 : 1
,, 29, ,, 1 ..	4·8	4·7+,,	13·8 . 1
,, 29, ,, 4 ..	3·3	3·5 ,,	21·0 : 1
,, 30, ,, 3 ..	7·1	7·4 ,,	9·9 : 1
,, 30, ,, 2 ..	5·5+	5·7−,,	18·4 : 1
,, 31, ,, 1 ..	10·5	10·5 ,,	7·1 : 1
September 5 ,, 1 ..	4·8	5·2 ,,	17·7 : 1
,, 5 ,, 2 ..	5·4	5·3 ,,	14·9 : 1
,, 5 ,, 3 ..	12·4	12·2 ,,	6·2 : 1
,, 5 ,, 4 ..	9·7	9·7 ,,	8·6 : 1
,, 6 ,, 1 ..	10·2	10·3 ,,	7·1 : 1
,, 6 ,, 3 ..	10·1	10·1 ,,	7·2 : 1
,, 7 ,, 2 ..	17·2	17·3 ,,	4·5 : 1
,, 7 ,, 1 ..	13·3	13·9 ,,	5·2 : 1

The results are so grouped around 100 per cent that the method is shown to be practically accurate—certainly for technical analysis. It will be noticed, however, that the tendency is to find more nitrous oxide than was taken; or, in other words, the contraction after running the gas over potassium hydroxide was greater than it should have been. From some later work, an account of which will appear in the communication to follow, I have found that the presence of a fraction of a drop of water in the grisoumeter causes striking results. The water is vaporised by the heat of the glowing spiral, and a reaction takes place by which the water is decomposed, the oxygen uniting with the carbon monoxide to form carbon dioxide, and the hydrogen going free. This causes an increase in the volume of gas after combustion, which does not take place in the absence of an excess of water vapour

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* Hempel, *Berichte*, 1882, p. 910.

† For description, see Hempel's "Methods of Gas Analysis," translated by Dennis; Macmillan, 1892, p. 236.

above that which is necesary to saturate the gases. The reaction is probably expressed by the following:[*]—

$CO+H_2O=CO_2+H_2$.[†]

On running the gases over potassium hydroxide, the carbon dioxide formed in this reaction is absorbed with the carbon dioxide formed from the oxygen of the nitrous oxide; but in the reaction with the water, for every volume of carbon monoxide transformed into carbon dioxide, and thereby rendered absorbable, there is a volume of hydrogen left which exactly replaces it, so the result comes out even. The hydrogen set free in this reaction may possibly unite with the nitrogen set free by the reduction of the nitrous oxide, and ammonia may be formed, as in the experiments with hydrogen; or, indeed, other condensation products may be formed. At the time these experiments were made I was not aware of this reaction between carbon monoxide and water, so that I did not note whether or not a fraction of a drop of water had gotten into the grisoumeter. In some experiments, however, I know this to have been the case, for after a partial combustion or an explosion I would run the gases over the potassium hydroxide, and after running them into the burette would then pass them back into the grisoumeter for a second combustion. In these instances I always got a small amount of the potassium hydroxide solution in the top of the capillary of the measuring burette, and sometimes a small particle of the liquid would be carried into the grisoumeter. I think it more than likely that working with a grisoumeter which thus contained an excess of moisture will account for the tendency of some results to come about 0·1 c.c. or more too high, while hardly any fall below.

One very great advantage of this method is that when the amount of nitrous oxide is small, it may be diluted with a large amount of carbon monoxide for convenience of manipulation, and still give good results from combustion. The most satisfactory results and the smoothest and quickest reaction is obtained when approximately,—

$$CO : N_2O :: 7 : 1.$$

If there is less carbon monoxide the mixture explodes, and when the excess of carbon monoxide is large it takes a longer time for complete combustion. It is always best to give a combustion of at least three to five minutes. Unless excess of moisture be present there are no side reactions, and no evidence of condensation products even after a combustion of an hour.

The experiments referred to in the present communication were carried on in the Hoagland Laboratory of Brooklyn, and at the Physiological Laboratory of the Johns Hopkins University during my connection with those laboratories. In addition to this, through the courtesy of Professor Morse, I was able to avail myself of the facilities of the Chemical Laboratory of the Johns Hopkins University, and through the courtesy of Profs. Dennis and Orndorff of Cornell University, I was invited to make use of the facilities of their laboratories while spending my vacation at Ithaca. It was there that the work was brought to a successful termination. It gives me pleasure to express my obligation to these gentlemen for the said courtesies, as well as for useful suggestions from time to time. I am also indebted to Mr. B. S. Cushman, of Cornell, for much valuable assistance.—*Johns Hopkins University Circular*, xiv., No. 116.

Chemical Society Anniversary.—The Anniversary Dinner of the Chemical Society will be held at the Hotel Métropole on Wednesday, March 27th, at 7 p.m. Fellows who wish to be present are requested to communicate with the Secretaries at Burlington House without delay.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 22nd, 1895.

Capt. Abney, F.R.S., President, in the Chair.

Messrs. W. R. Cooper, J. H. Gardiner, and J. W. Rodger were elected members of the Society.

An abstract of Mr. G. H. Bryan's paper on "*The Mechanical Analogue of Thermal Equilibrium between Bodies in Contact*" was read by Mr. Elder.

After commenting on the difficulty in applying the kinetic theory of gases to the case of two substances in contact which do not mix, the author goes on to describe a system by which the phenomena of thermal equilibrium unaccompanied by diffusion can be explained.

The two substances are represented by two sets of molecules, designated by P and Q. Two parallel planes, A and B, at a small distance apart, are imagined to divide space in three parts. Plane A (to the left of B) is supposed to be permeable to the P molecules, but to repel the Q molecules; whilst B is permeable to the Q set of molecules and repels the P set. The spaces to the left of A and to the right of B are thus entirely occupied by the P and Q molecules respectively. Between the planes both P and Q molecules exist, and therefore have opportunities of colliding with one another, and transferring energy from one gas to the other.

Using generalised co-ordinates, it is shown by Boltzman's method that when equilibrium is attained the mean kinetic energies of translation of the two kinds of molecules are equal, just as in the case of molecules which mix.

Instead of assuming the planes A and B to repel the Q and P molecules respectively, the P molecules may be assumed to be positively electrified, and the Q ones negatively electrified; whilst the planes A and B are maintained at a constant difference of potential. The difference of potential thus assumed is analogous to "contact E.M.F.," whose existence is proved by experiment.

The communication concludes with a development of Prof. Boltzman's paper "On the application of the Determinantal Relation to the Kinetic Theory of Polyatomic Gases," read before the British Association at Oxford.

Dr. Stoney thought the arguments were based on actions depending on the distances of the molecules and the supposition that they were rigid. In his opinion events occur in nature which are not represented by this simple theory, and great reservation should be shown in accepting dynamical problems which leave out of account actions occurring between matter and the ether. In nature nothing was large and nothing was small except relatively. Even molecules might possess infinite detail of structure. Their interaction with the ether must be considered in any complete theory.

Mr. G. V. Yule's paper "On a New Harmonic Analyser," and one by H. N. Allen "On the Electromagnetic Field," were postponed.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Dr. McDonald in the chair.

The sixth meeting of the Society for the present Session was held on February 11th.

Mr. A. Forbes Watson read a paper on "*Argon.*"

He gave a connected account of the circumstances which led to the discovery of the gas, and described the methods by which it had been isolated. Particular attention was paid to the question of ratio of specific heats and to the place which the element could occupy in Mendeleeff's table.

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[*] Dixon, *Phil. Trans.*, 1884, and *Journ. Chem. Society*, 1886.

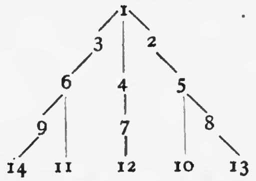
[†] In my own experiments I have shown the presence of free hydrogen by absorption with palladium.

NOTICES OF BOOKS.

The Genetic System of the Chemical Elements. By W. Preyer. With a Lithographed Table. Berlin: Friedlander and Son. 1894.

The author informs us in his preface that his system includes the families of Mendeleeff's natural system and Lothar Meyer's periodic law, and retains the septimal division first recognised by Newlands. But on considering this system, as well as Wendt's pedigree of the elements and the spiral of Reynolds and Crookes, he finds that some modifications are needed to agree with reality. In his new pedigree of the elements he shows that a series of properties mutually independent are brought into systematic connection. He traces this connection in ten different directions, and hopes that his hypothesis of the derivation of the elements of high atomic weights from those of low ones, and ultimately from an extremely finely divided primitive substance—in fact, protyle—may soon claim the rank of a theory.

He gives the pedigree of the elements according to the following scheme, including fourteen gradation numbers.



Here 1 signifies any one of the seven elements following upon hydrogen in a series arranged arithmetically according to the atomic weights, and at the same time divided into periods of seven members. These elements have been produced according to hypothesis by one condensation. Hence,—

1. Li, Be, Bo, C, N, O, F.

Each of these seven elements, which form the first stage of condensation and represent the first generation in the pedigree, yields on further condensation a second denser stage, *i.e.*,—

2. Na, Mg, Al, Si, P, S, Cl.

Each of the less dense elements 1 underwent a further condensation, forming the elements—

3. Ka, Ca, Sc, Ti, Va, Cr, Mn.

A corresponding process of condensation is carried on through five generations, and thus the author includes in his complete system all the known elements and fifteen which are probable.

Professor Preyer seeks the evidence for his hypothesis in the atomic weights, in the differences of the atomic weights, in the specific gravities, the atomic volumes, the specific heats, the atomic heats, the volume heats, the electro-chemical tensions, the magnetic phenomena, and in valence. Many of the attributes in certain elements have not been determined with satisfactory accuracy. But we may admit that the general consensus of the evidence adduced seems favourable to the views of Prof. Preyer.

Treating of the unknown elements, the author places their number, as an outside estimate, at fifteen. Their properties are, of course, a matter of conjecture. We find the very justifiable remark that all the specimens used for the determination of such points must be absolutely pure. In this respect there is room for delicate and accurate research enough to engage the life-time of not a few zealous and well qualified experimentalists. To such investigations we beg to draw special attention.

Cod Liver Oil and Chemistry. By F. Peckel Möller, Ph.D. London: Peter Möller, 43, Snow Hill, E.C.; and at Christiana, Norway.

This curiously entitled work consists of parts which do not exactly appeal to the same class of readers.

The first portion, paged with Roman numerals, addresses mainly the pharmacist and the physician.

The second and larger section, paged in the ordinary Arabic numerals, claims the attention of the pure chemist.

Into the consideration of the first part we can scarcely enter. We may, however, note that, among the fishes of the Norwegian coast, the halibut has been overlooked, though it reaches an immense size, and, save for the production of oil, it far surpasses the cod. The dangers of the Lofoten fishery are serious. It is here recorded that some years ago 500 fishermen perished in a single day!

In the history of the cod-liver oil trade an epoch has been made by the introduction of the extraction by steam, due to Peter Möller, in 1853.

It is clearly and truthfully shown that the natural colour of cod-liver oil is a very pale yellow, and that the brown qualities, light or dark, owe their colour to decomposition. The most recent improvement devised consists in performing the extraction process in a current of carbonic acid gas, atmospheric air, and consequently oxygen, being excluded. The rancidity of the brown oils is now proved to be due not to free acids, but to the formation of hydroxy-acids. It is interesting to note that persons interested in the brown oil trade calmly assert, in the face of all evidence, that the colourless oils have been artificially bleached. Dr. Möller gives the conditions to be observed if an ideal oil is to be obtained. One of these is that the livers should be perfectly fresh. This is the reason why the Norwegian oils are superior to all others. At the Lofotens the cod are caught close to land, and can be conveyed to the factories before putrefaction has set in. This is not, *e.g.*, the case off Newfoundland.

The purely chemical portion of Dr. Möller's book bears the title—"The Law of Atomic Linking Diagrammatically Illustrated." It is, in fact, a treatise on organic chemistry expressed in graphic formulæ to a most unusual degree. His formulæ showed him why the attempt to form antipyrine by causing a derivative of butyric acid to react upon phenylhydrazin was a failure; the product being, in fact, iso-antipyrine. Another novel view relates to the difference between uric acid and xanthine. Both these substances may be looked upon as consisting of two mols. of urea and one of acrylic acid. The difference between them is that in the one case the acrylic acid turns its extremities towards the urea in a different manner to the other.

Of more importance is the suggestion put forward to explain the rotation of polarised light. Like Baeyer, he is not satisfied with the banal explanation of this phenomenon by the presence of a non-symmetric carbon. The author's own hypothesis does not well admit of statement without the diagrams of succinic acid, dextro-tartaric acid, lævo-tartaric acid, and meso-tartaric acid.

The only objection which we can find to Dr. Möller's method of expounding organic chemistry is that the diagrams which are necessary at every step must be exceedingly costly. If he could find some method of expounding, *e.g.*, his views on the cause of rotatory polarisation without diagrams, his treatise would, we feel sure, be widely read.

The author has little cause to apologise for his English; it is racy, flowing, and idiomatic, enlivened at times with a dry humour which somewhat reminds us of our late friend Dr. Angus Smith.

Action of Picric Acid and the Picrates upon the Mercuric Cyanides. The Isopurpurates.—Raoul Varet.—The author has studied methodically the action of picric acid and of the picrates, on the one hand, upon potassium, sodium, lithium, barium, strontium, calcium, magnesium, cadmium, and zinc cyanides, all of which form isopurpurates. On the contrary, the mercury, copper, and silver cyanides are not decomposed by a solution of picric acid, even if boiling, and they do not yield isopurpurates.—*Bull. de la Soc. Chim. de Paris*, No. 22, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 6, February 11, 1895.

On the presence of Alumina in Plants and on its Distribution.—M. Berthelot and G. André.—The determinations given by the author show that alumina may exist in the ash of annual plants provided with plentiful and deep roots. Its proportion in the analysis of other lucern is comparable to that of the other bases; it coexists with phosphoric acid. But immediately after its absorption (or fixation) by the roots it is arrested. It arrives at the leaves only in a minimum proportion, and in the case of a tree, such as the lime, in a proportion almost infinitesimal. Alumina, as well as aluminium phosphate, may be kept in solution and then absorbed in presence of citric and tartaric acids.

Preparation and Properties of Titanium.—Henri Moissan.—(See p. 103).

Report on a Memoir by E. Hardy relating to the Application of Sonorous Vibrations to the Analysis of two Gases of Different Specific Gravities.—In detecting the proportion of "fire-damp" contained in the air of a coal mine, E. Hardy makes use of a purely physical property, the decrease of sp. gr. which air undergoes in consequence of an admixture of fire-damp. The method is founded on the fact that any variation in the density of a gas feeding a sounding-pipe is shown by a variation in the pitch of the sound produced. As this variation in pitch becomes very sensible by the production of beats, Hardy utilises it for determining the volume of the fire-damp (formene) by means of an apparatus which he names the *formenophone*. It is necessary to exclude from the specimens operated upon all carbonic acid and watery vapour. The Commissioners express themselves perfectly satisfied with the memoir as showing the way for a continuous and systematic record of the proportion of fire-damp present in the air of a mine.

Lowering of the Freezing-points of Dilute Solutions of Sodium Chloride.—A. Ponsot.—This memoir requires to be accompanied by the table and the diagram here given.

Gold Sulphide.—A Ditte.—This paper will be inserted in full.

Method for Determining the Crystallisation of Precipitates. Zinc and Manganous Sulphides and Copper Hydroxide.—A. Villiers.—This memoir also will be inserted in full.

Cinchonigine: Dimorphism of a Compound presenting Specific Molecular Rotatory Power.—E. Jungfleisch and E. Léger.—The two forms of cinchonigine are easily converted into each other. The klinorhombic form is stable at the ordinary temperature, whilst the orthorhombic form is stable at the boiling temperature of ether, about 35°. Except strontium acid tartrate, cinchonigine is the first instance of a dimorphous substance possessing a specific molecular rotatory power.

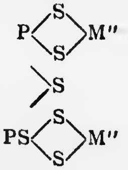
Plurality of Chlorophylls. A second Chlorophyll isolated in Lucern.—A. Etard.—A given vegetable species may contain several chlorophylls. It is convenient to give to each of these pigments isolated chemically a name derived from the botanical name of the plant with an index. Lucern contains among other chlorophylls, medicagophyll-α, $C_{28}H_{45}NO_4$, and medicagophyll-β, $C_{42}H_{63}NO_4$. Certain chlorophylls soluble in pentane are, by their scission, the instruments of the chemical production of essences and oils. Others, insoluble in carbides, tend, on splitting up, to produce carbon hydrates, tannins, and extracts.

Comparison between the Coloured and the Colourless Derivatives of Hexamethyltriamidotriphenylmethane.—A. Rosenstiehl.—In a former paper we have considered three colouring matters and eleven colourless substances all containing the group $[(CH_3)_2NC_6H_4]_3\equiv C$, which we represent more simply by $A_3\equiv C$. The colourless bodies are divided into two classes, according as they are or are not convertible into colouring matters by means of double decomposition. The coloured substances are characterised by the presence of a negative radicle Cl,I (or, in general, of an acid radicle) united to a methanic carbon. With the latter they have in common an amidised phenylic group in para which satisfies the three other valences of the methanic carbon. In this group the nitrogen is not saturated, but has the function of a trivalent element.

On an Ether of a New Genus. Methylene Lactate.—Louis Henry.—This is a colourless liquid, mobile, of a strong odour, resembling that of methanal and of an extremely pungent taste. Its sp. gr. at 2·5° = 1·1974. It boils at 153—154° under a pressure of 754 m.m. Its vapour-density is 3·47. Its melting-point is −28°. It is insoluble in cold water, but in hot water it dissolves with decomposition.

Bulletin de la Société Chimique de Paris. Series 3, Vols. xi.-xii., No. 22, 1894.

New Series of Sulphophosphides: the Thiohypophosphites.—C. Friedel.—The author describes the iron, aluminium, zinc, copper, lead, silver, mercury, stannic and stannous compounds of the acid. As the general formula of these salts he gives—



Action of Thionyl Chloride upon the Oxalic and Formic Acids.—Ch. Moureu.—Thionyl chloride reacts upon the oxalic (oxalates) and formic acids in the manner of sulphuric acid; that is, as a dehydrating agent, passing itself to the state of sulphurous and hydrochloric acid (or chloride).

Action of Thionyl Chloride upon the Aldoximes. Formation of Nitriles.—Ch. Moureu.—We see that thionyl chloride when reacting upon the aldoximes behaves like acetic anhydride; it withdraws from these substances 1 mol. of water, and yields nitriles according to the general equation—

$$R-CH=NOH+SOCl_2=SO_2+2HCl+R-CN.$$

Determination of Mannite in Wines.—J. A. Müller.—This paper will be inserted in full if practicable.

Synthesis of Selenised Aromatic Compounds.—C. Chabre.—A controversial paper in reply to the strictures of Kraft and Vorster.

Determination of Phosphorus in Products of the Metallurgy of Iron.—P. Benazet.—Certain portions of this extensive 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.

Evaporative Power of Coal.—Can any of your readers give me a short and simple receipt for arriving at the evaporative power of a given quantity of coal, say 1 cwt.? Can anyone suggest a work treating on this point plainly?—Subscriber.

Erratum.—P. 79, col. 2, line 20 from top, *for* "hydrogen" *read* "hydrazine." Line 30, *for* "A .. −137°" *read* "A .. −187°."

MEETINGS FOR THE WEEK.

Monday, 4th.—Society of Chemical Industry, 8. "The Durability of Pigments derived from Coal-Tar," by A. P. Laurie, F.C.S. "The Hermite System of Sewage Purification," by Sir Henry Roscoe, F.R.S., and Joseph Lunt, B.Sc.

Tuesday, 5th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "Colonies and Treaties," by Sir Charles M. Kennedy, C.B.

Wednesday, 6th.—Society of Arts, 8. "Cider," by C. W. Radcliffe Cooke, M.P.
— Institution of Mining and Metallurgy, 8. Discussion on "Some Improvements in Gold Extraction. Followed by Papers.
— Geological, 8.

Thursday, 7th.—Royal, 4 30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Three Periods of 17th Century History—I. The Stuart Monarchy," by Samuel Rawson Gardiner. M.A.
— Chemical, 8. "Dimethylketohexamethylene," by Dr. Kipping.

Friday, 8th.—Physical, 5. Exhibitions—By Mr. Nabir, of a Voltameter. By Dr. G. Johnstone Stoney, F.R.S., The Focal Heliostat; An Improvement in Siderostats. "On a New Harmonic Analyser," by G. V. Yule. "On the Electromagnetic Field," by H. N. Allen.
— Royal Institution, 9. "The Physical Work of Von Helmholtz," by Prof. A. W. Rücker. M.A., F.R.S.
— Astronomical, 8.
— Medical, 7. (Annual Dinner).

Saturday, 9th.—Royal Institution, 3. "Waves and Vibrations,' by Lord Rayleigh, F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXI., No. 1841.

NOTE ON THE SPECTRUM OF ARGON.*

By H. F. NEWALL.

In the course of a spectroscopic investigation in which I have been for some time past engaged, a line spectrum, which so far as I was able to make out, was unknown, has frequently presented itself upon my photographs. It appeared in May and June, 1894, under conditions which led me to call it, for the sake of convenience, "the low-pressure spectrum." After their announcement at the Oxford meeting of the British Association, it seemed for many reasons natural to borrow the first letter of Lord Rayleigh's and Professor Ramsay's names to give to the unknown lines, and in the measurements of the photographs which showed the lines well there appears an "R" against seventeen lines out of sixty-one measured, the remaining lines being known to belong to Hg, H, N, and nitrocarbons. It transpires now, as I learnt from reading the abstract of the paper in which Lord Rayleigh and Professor Ramsay describe their consummate researches on argon, that the symbol "A" should have been used instead of "R" to designate the lines on my photographs. For the lines are argon lines.

The conditions under which the spectrum of argon has appeared in my investigations are of interest at the present time, and I hope a description of them may not be unacceptable.

A glass bulb was sealed hermetically to a mercury pump of the Hagen-Töpler form, in which there was strong sulphuric acid floating on the surface of the mercury. The bulb was exhausted as low as possible and refilled with air. The pressure was reduced to about 180 millionths of an atmosphere (=0·14 m.m.), at which pressure a bright discharge could be passed through the residual gases by means of Professor J. J. Thomson's method of surrounding the bulb by a coil of wire, which carries a very rapidly alternating current produced by the discharge of a condenser.

The discharge was passed for thirty minutes, during which time a photograph of the spectrum was taken. The pressure of the gas in the bulb fell during the passage of the discharge from the value 174 M (=0·13 m.m.) to 112 M (=0·085 m.m.), The spectrum shows the bands of nitrogen strong, also mercury lines and nitrocarbon groups strong, hydrogen weak, no oxygen or argon.

Again the discharge was passed for thirty minutes and a new photograph was taken. The pressure fell from 100 M (=0·076 m.m.) to 20 M (=0·015 m.m.); the nitrogen spectrum had faded considerably, and there had appeared a number of fine lines which I was unable, in spite of careful efforts, to identify with the lines of any known substances.

The nature of my method of investigation of spectra is such that it is not difficult to pick out of the numerous spectra which appear superposed on the photographic plate the lines which belong to any one spectrum. (The photographic re-productions attached show clearly the ease with which this may be done).

The results of measurement made in the last few days of seventy-two lines in my "low-pressure spectrum" are given below, and side by side are given the measurements of the wave-lengths determined by Mr. Crookes for the argon lines.

The agreement of the measurements shows conclusively that we have been measuring the same spectrum. Be-

Table of Wave-lengths.

H. F. Newall. William Crookes. Jan. 24, 1895.

The Two Spectra of Argon.

Measurements of lines on photograph.		Blue.		Red.	
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Inten.
4879·8	5	487·9	10	487·9	4
4847·2	5	484·75	1		
4808·0	9	480·50	7		
4766·6	5	476·30	1		
4738·0	8	473·45	6		
4729·4	6	472·66	2		
				470·12	8
4659 6	7	465·65	5		
4644·0	1				
4639·0	2				
4632·1	4			462·95	5
4611·0	9	460·80	8		
4592·0	8			459·45	2
		458·69	6		
4581·2	6	457 95	6		
4546·5	7	454·35	7		
				451·40	2
		450·95	8	450·95	9
4482·2	6	447·83	6		
4460·0	2				
4431·3	10	442·65	10		
4426·0	10	442·25	10		
4421·2	4				
4414·1	4				
4401·7	9	439·95	10		
4400·1	5				
4379·8	8	437·65	9		
4375·8	3				
4370·4	8	436·90	9		
4351·4	7	434·85	10		
4336·0	2			434·50	5
4330·8	10	433·35	9	433·35	9
4308·7	4			430·05	9
4299·4	4	429·90	9		
4282·1	6				
4277·4	8 ? N	427·70	3		
		427·20	7	427·20	8
4266·4	9 ? N	426·60	6	426·60	4
		425·95	8	425·95	9
		425·15	2	425·15	3
4227·5	8	422·85	6		
CN group has, though only of intensity 5, obliterated this set of lines.		420·10	10	420·10	10
		419·80	9	419·80	9
		419·15	9	419·15	9
		418·30	8	418·30	8
		416·45	8	416·45	4
		415·95	10	415·95	10
4155·8				415·65	6
4130·9	6	413·15	3		
4104·2	8	410·50	8		
4082·2	4				
4075·8	3				
4072·4	9	407·25	8		
4069·7	2	404·40	8	404·40	9
4042·7	5				
4038·2	5				
4035·0	2				
4033·7	3	403·30	1		
4013·8	8	401·30	8		
3994·8	6				
3991·3	4				
3979·2	3	397·85	1		
3973·0	4				
3968·0	7	396·78	3		
		394·85	9	394·85	10
3944·1	5	394·35	3		
3932·3	5				
3930·8	3	393·18	3		

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* A Paper read before the Royal Society, February 21, 1895.

Measurements of lines on photograph.		Blue.		Red.	
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Inten.
3928·2	8	392·85	9		
3920·3	6				
3918·8	5	392·75	3		
		391·50	1		
3892·2 ?	—			390·45	8
3883·2	5	389·20	5		
3873·4	4	387·55	2		
		387·18	2		
3868·1	6	386·85	8		
3850·8	7	385·15	10		
		384·55	1		
		383·55	2	383·55	3
3827·0	—	382·75	2		
3809·8	4	380·95	4		
		380·35	1		
		379·95	1		
3781·8	6	378·08	9	377·15	1
		377·05	2		
3766·1	5	376·60	8		
3750·2	3				
3738·8	3	373·85	3		
3730·0	8	372·98	10		
3719·2	2	371·80	4		

tween $H\gamma$ and wave-length 370, the agreement is all that we could hope for, taking into account the fact that my measurements were not made with a view of giving a final and carefully-considered set of measurements of wave-lengths, but between $H\gamma$ and $H\beta$ there is a systematic difference of about 3 tenth-metres, which I am unable at present to account for. The agreement of grouping and intensity, however, leaves no doubt as to the identity of the spectrum of my low-pressure lines with the spectrum of argon. I have reduced my measurements with reference to Rowland's scale of wave-lengths, and I infer from the value adopted for the $H\beta$ (F) line that Angström's scale has been used in Mr. Crookes's reduction. The difference between the scales is not enough to account for the discrepancies above referred to.

The experiments were repeated, with slight variations, several times, with results which, so far as the spectrum of argon is concerned, were constant. But it was noted that continued passage of the discharge appears to result in the attaining of a certain minimum pressure, after which there is slight and slow rise to a tolerably-fixed pressure. It is not necessary to dwell on these points in the present note.

It is interesting to find argon asserting itself, unsolicited, in quite new circumstances, and under conditions which practically constitute one more mode of separating argon from nitrogen—namely, the getting rid of nitrogen by passing electric discharge through it in the presence of hydrogen or moisture and acid.

REMARKS ON THE ATOMIC WEIGHTS.

By LECOQ DE BOISBAUDRAN.

For a long time I have been engaged in studying the relation among the atomic weights of the elements, and if I have not yet published my attempt at the classification of the simple substances it is because this investigation presents great difficulties, and because errors are easily committed. We sometimes meet with interesting relations on classifying the elements according to systems which are not merely different, but incompatible.

Such as it was some years ago, it gave me the atomic weight of gallium with a very satisfactory exactitude, and it has enabled me to modify happily the atomic weight of germanium, which had then been provisionally determined by Prof. Winkler upon a specimen which was imperfectly purified.

These two successes will, I hope, serve as my excuse to the Academy if I venture to submit to it certain deductions from my theory which seem to connect themselves with the question of argon.

This substance, so brilliantly discovered by Lord Rayleigh and Prof. Ramsay, may perhaps take its place in a family of elements no member of which is hitherto known.

This family, whose existence my classification enables me to assume should be of a non-metallic nature, and should comprise elements having the atomic weights—20·0945; 36·40 ± 0·08; 84·01 ± 0·20; 132·71 ± 0·15, if we assume arbitrarily O = 16.

The atomicity of the new family should be even (octo-atomic), but its component elements should be devoid of the faculty of combining with other elements.

The bodies 20·0945 and 36·40 should be relatively abundant in Nature, but 84·01, and especially 132·71, should be rare.

The element 36·40 should be more volatile than sulphur, and the element 20·0945 more volatile than oxygen. Lastly, the elements 84·01 and 132·71 should be respectively more volatile than selenium and tellurium.

At the moment of presenting this note to the Academy I read, in the *Revue Generale des Sciences*, the memoir of Lord Rayleigh and Prof. Ramsay, and I see that these *savants* have thought of attaching argon to the eighth rank in the classification of Mendeleeff. It seems to me that they are perfectly right. The considerations according to which I have presupposed the existence of a new family, non-metallic and octo-atomic, are not the same as those which have led Prof. Mendeleeff in his classification, but they are far from being contradictory. These are different points of view which enable us, I believe, to see different aspects of the same truth, and each of which presents special advantages.

My classification claims the advantage of permitting a calculation of the atomic weights, exact or closely approximate.—*Comptes Rendus*, cxx., p. 361.

HOW TO PREPARE ARGON ON A LARGE SCALE.

By BOHUSLAV BRAUNER, Ph.D.,
Late Bishop Berkeley Fellow of Owens College.

I have not yet ceased to study Lord Rayleigh's and Dr. Ramsay's paper on Argon, and I well consider the difficulties connected with the isolation of that new gas. A hard work of more than one week is necessary to obtain half a litre of the gas, *i.e.*, 1 grm. (560 c.c. weigh 1 grm.).

The method of diffusion was tried by the authors for an accumulation of the gas, but it does not seem to be promising much. I think the reason is this:—

The rate of diffusion of gases is inversely proportional to their molecular weight. Now the molecular weight of argon is A = 40 when O = 32 and N = 28, and the theoretical coefficients of diffusion will be A = 0·894, O = 1·000, N = 1·069. These numbers differ enough as to promise a good result, and yet they will hardly be confirmed by experiment, for the following reason:—

Argon *is*, or at any rate behaves physically as, a monatomic gas, and we must therefore suppose that its single atoms will pass more easily through the pores of membranes than would correspond to its calculated diffusion coefficient, and that it will meet, on its passage through the pores, with far less obstacles than a diatomic or polyatomic gas molecule of the same weight, owing to the greater distance of atomic centres in the latter. It will be, therefore, only slightly more accumulated in the air which has *not* diffused through the churchwarden tobacco-pipes—as proved by experiment. Of course it must be considered that the unknown *coefficient of transpiration* plays an important *rôle* at the same time.

A much better result might be expected from the property of argon, being 2½ times more soluble in water than nitrogen (Rayleigh and Ramsay). Large quantities of argon will be needed for the complete study of its physical, chemical, and physiological (biological) properties, especially of its behaviour against organisms (repetition of Priestley's work from a modern point of view) and micro-organisms, as pointed out by Berthelot and the author of the present lines simultaneously. This is all impossible, unless it becomes practicable to prepare argon on a large scale.

Let us consider the following :—

In the year 1870, Mallet (*Dingl. Pol. Journ.*, 199, 112; *Journal fur Gasbereitung*, 1870, 538) had established an industrial method of preparing oxygen from the atmospheric air upon the property of water of absorbing oxygen more eagerly than nitrogen. By means of the apparatus described (*loc. cit.*) air is pumped into water under large pressure; the absorbed gases are liberated, and pumped again into water. After repeating this process eight times, a gas is obtained which consists of 97·3 parts of oxygen and 2·7 parts of nitrogen.*

I have no doubt that this last is nearly pure, or at least highly accumulated argon, and that this method will prove effective for the production of "crude argon," especially if oxygen be removed first,—*e.g.*, only technically,—by passing the air over red-hot iron turnings.

I know the munificence of rich intelligent Englishmen, and I think I am not mistaken in supposing that a possessor of chemical works—*e.g.*, the generous supporter of chemico-physical research, and founder of the "Davy-Faraday Research Laboratory"—would be able to establish a plant for the production of "crude argon" on a large scale, on the above plan, and store it in Brin cylinders, which would greatly help the study of one of the most important scientific problems.

Though a "pure scientist" I may be allowed to mention the possible first practical application of argon, which will be undoubtedly for filling Geissler tubes as described by Mr. Crookes. Such articles would find enormous sale amongst the many chemical and physical institutions and laboratories, and the not smaller number of scientific workers and amateurs of the whole world.

I shall be glad if the above lines should prove a step towards the solution of the problem in question.

Bohemian University, Prague,
February 28, 1895.

ACTION OF PHOSPHORUS PENTACHLORIDE UPON α-BENZOYLPHENYLHYDRAZIN.

By H. v. PECHMANN and L. SEEBERGER.

On heating symmetrical benzoylphenylhydrazin with phosphorus pentachloride, the authors obtained, besides the imid-chloride of the latter, a series of compounds which on examination have been chiefly identified as benzoylised hydrazides of phosphoric acid. Among these compounds are—

1. *Chloromethylbenzenphenylhydrazon*,—

$C_6H_5CCl.N.NHC_6H_5$.

This compound is characterised by the following reactions:—Insoluble in soda-lye; turned to a blue-green by concentrated sulphuric acid and ferric chloride. An especial characteristic is the formation of red crystalline needles of formazylbenzol if the alcoholic solution is brought in contact with phenylhydrazin at the common temperature.

2. *Lactone of s-Benzoylphenylhydrazid phosphoric Acid.*—This compound has the composition $C_{13}H_{11}N_2PO_3$. It melts at 161°. Readily soluble in alcohol, insoluble in water. Readily taken up by soda-lye. Solution in concentrated sulphuric acid is slowly rendered blue by ferric chloride. Solution in concentrated sulphuric acid does not reduce mercury oxide. A distinction from *s* benzoylphenylhydrazin and—

3. *s-Disbenzoylphenylhydrazido phosphoric Acid*,—

$C_{261}H_{23}N_4PO_4$.

This compound crystallises from methylic alcohol in prisms of a vitreous lustre or felted needles; melting-point 131—132°. It is soluble in soda-lye. The solution in concentrated sulphuric acid is rendered violet by ferric chloride. The solution in chloroform reduces mercury oxide in the cold (rendering the presence of two imido-groups probable). Hot concentrated sulphuric acid splits it up into phosphoric acid and benzoylphenylhydrazin.

4. *Lacton of s-Disbenzoylphenylhydrazido-phosphoric Acid.*—This compound, $C_{26}H_{21}N_4PO_3$, is insoluble in soda-lye. The sulphuric solution is slowly turned red by ferric chloride. If boiled with glacial acetic acid, is split up into phosphoric acid and benzoylhydrazin. The solution in chloroform does not reduce mercury oxide.

5. On heating *s*-benzoylphenylhydrazin with phosphorus pentachloride for some hours, a compound is obtained which is not yet named. Its composition is probably similar to that of No. 4. It contains 11·8 per cent N and 7·0 per cent P. It melts at 220°. Insoluble in soda-lye. Solution in concentrated sulphuric acid is gradually turned red by ferric chloride. Permanent with mercury oxide.—*Berichte*, xxvii., p. 2123.

THE ACTION OF PHENYLHYDRAZIN UPON ETHOXYMETHYLENMALONIC ETHER.

By L. CLAISSEN and C. HAASE.

Malonic ether combines easily with orthoformic ether to ethoxymethylenmalonic ether.

We have treated this ether with phenylhydrazin, and ultimately arrived at phenylpyrazolon, with the melting-point 118°. A discussion on the constitution of this substance has arisen between Stalz, von Rothenburg, and Ruhemann and Morrell. Stalz regards the substance fusible at 118° as (1)-phenyl-(5)-pyrazolon, and that fusible at 153° as (1)-phenyl-(3)-pyrazolon, whilst the conclusion of von Rothenburg is exactly opposite. From what follows we are compelled to accept the view of Stalz as correct.

1. *Phenylhydrazid or Phenylhydrazon*, when purified, melts at 112°; it dissolves easily in alcohol, acetone, benzene, chloroform, and acetic ether, but less readily in alcohol. Its composition is $C_{14}H_{18}N_2O_4$.

2. *Phenyl-(5)-pyrazolon-(4)-carbonic Ether.*—Its sodium salt crystallises from hot water in fine shining needles. From its aqueous solution acetic acid throws down pyrazolon carbonic ether as a white precipitate. After drainage we dissolved it in hot alcohol, and added water to incipient turbidity. After standing for some time and evaporation, the ether separated in long white silky needles, fusible at 117—118°. It is slightly soluble in water, readily soluble in alcohol, ether, acetone, and benzene. The alcoholic solution is coloured a deep red by ferric chloride.

3. (1)-*Phenyl-(5)-pyrazolon-(4)-carbonic Ether.*—Its percentage composition is—

C	58·82
H	3·92
N	13·73

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* On representing the decrease of the percentage of oxygen after each operation *graphically*, a curve is obtained, which shows clearly that after several operations the absorption coefficient of "atmospheric nitrogen," which is then rich in argon, approaches that of oxygen.

It melts at 92—93° with an escape of gases. It is distinguished from the very stable (1)-phenyl-(5)-pyrazolon-(3)-carbonic acid of Wislicenus by the readiness with which it splits off carbonic acid on boiling with water, or more closely on keeping. This instability of the acid depends on the position of the carboxyl group, which occupies a place similar to that in acet-acetic acid.

4. (1)-*Phenyl*-(5)-*pyrazolon* may be obtained directly from the carbonic ether by dissolving it in so much soda-lye that to each mol. of the ether there are present at least 3 mols. of soda-lye. The solution, after being heated for some hours on the water-bath, is precipitated with hydrochloric acid, and then heated until the escape of carbonic acid has ceased. As it cools, the pyrazolon deposits as a white mass. After purification it crystallises in colourless flat prisms, melting at 118—119°. The pyrazolon has the composition $C_9H_8N_2O.HCl$. In its behaviour it agrees completely with Knorr's (1)-phenyl-(3)-methyl-(5)-pyrazolon. With ferric chloride it gives Knorr's pyrazol-blue reaction very distinctly. This reaction is best obtained by dissolving a very little pyrazolon in a few c.c. of boiling water, and carefully adding to the hot solution a very dilute solution of ferric chloride (at most 4 per cent). The blue obtained from the above pyrazolon is of a more violet shade than that from phenylmethylpyrazolon.

The above pyrazolon yields with benzaldehyd a benzal compound; with nitrous acid an isonitroso-derivative. The former forms reddish yellow flattened needles, melting at 170°. The isonitroso-compound crystallises in tender needles of an orange colour, which melt at 160° with decomposition.

The authors conclude their paper with a full discussion of the structural formulæ which have been proposed for pyrazolon, and ascribe the preference to that of Stalz.—*Berichte*, xxviii., No. 1, p. 35.

ON THE

PHOTOGRAPHY OF THE LIGHT RAYS OF THE SMALLEST WAVE-LENGTHS.*

By Dr. VICTOR SCHUMANN.

At the conclusion of my investigation on the photography of the luminous rays of the shortest wave-lengths (presented to the Imperial Academy of Sciences of Vienna in the year 1893), I promised as a continuation the solution of several problems there specially indicated. As the preliminary researches commenced a year ago already afford a series of facts ripe for mention, I permit them to follow in as far as they relate to the rays of the shortest wave-lengths. A complete report on the entire results, along with the figures of the spectra obtained, will at no very distant date complete my present communications.

1. I have improved my ultra-violet sensitive plate and the process for its production so far that its sensitive coating may be produced in half an hour; that it works more sensitively and neatly than the former plate, bears the most powerful developers without injury, and can be made still more sensitive for the ultra violet by immersion in common water.

2. My vacuum spectrograph, after a modification recently undertaken, effects, whilst the sharpness of the spectra remains faultless, more in a few minutes than previously in hours.

3. The spectrum of hydrogen taken with my improved spectrograph and the new plate displays, as compared with former proofs, a further important increase in length.

4. The same holds good for the spectra of Fe, Co, Al, Zn, Cd, which previously extended only to the wave-length 170 $\mu\mu$. They are now but little inferior in extent to the spectrum of hydrogen. I have not yet been able to examine other spectra in this respect.

5. The limit of the spectrum above named, drawn close upon 170 $\mu\mu$, was a consequence of the impervious character of the air and of the vapour of the electrodes. The air only has been latterly found to be a little more transmissive than I formerly felt justified in assuming, but even in strata of very slight thickness (a few hundredths of a m.m.) it interferes to a great extent with the photographic action of the most refrangible rays. I have been able to trace its absorbent influence to far below a stratum of 0·01 m.m. in thickness.

6. Hydrogen in a dense layer visibly absorbs the most refrangible rays, and still more if imperfectly dried.

THE ACTION OF MAGNESIUM UPON THE VAPOURS OF THE ALCOHOLS,

AND A

NEW METHOD OF PREPARING ALLYLENE.*

By EDWARD H. KEISER and MARY B. BREED.

Under certain conditions magnesium is one of the most active elements. At high temperatures, as is well known, it has the power of reducing many of the most stable oxides, and in the absence of oxygen it can combine with nitrogen and form a nitride. That magnesium can also unite with carbon and form derivatives of the hydrocarbons will appear from the experiments described in this paper. An exhaustive study of the action of magnesium upon the oxides and hydroxides of the elements has been made by Winkler (*Ber. d. Deutsch. Chem. Ges.*, xxiii., 120, 772, 2642), and Seubert and Schmidt (*Liebig's Annalen*, cclxvii., 218) have studied its effects upon the chlorides of the elements. So far as we know, no one has hitherto examined systematically the action of magnesium upon organic compounds containing oxygen. Preliminary experiments showed us that when magnesium is heated with organic oxygen compounds, such as alcohols, acids, ketones, &c., a reaction, accompanied by an incandescence of the metal, takes place at more or less elevated temperatures. Thus far we have studied in detail the action of the metal upon several alcohols, and, as one of the results, have found a ready method of obtaining the unsaturated hydrocarbon allylene, C_3H_4.

The experiments were conducted as follows:—The magnesium, in the form of filings, was placed in a porcelain or iron boat, and heated in a combustion tube through which the vapour of the alcohol was passed. Before raising the temperature of the magnesium, the air in the apparatus was expelled by the alcohol vapour. At a low red heat the magnesium begins to glow at one end of the boat, and usually, after a few moments, it becomes red-hot throughout its entire mass. The boat and its contents are then allowed to cool down in the alcohol vapour. During the time that the magnesium is glowing, large volumes of gas are evolved from the tube. These gases were in each case collected in a gasometer, and subsequently analysed.

The first alcohol examined was methyl alcohol. The magnesium, at a low red heat, acts energetically upon it. After cooling, the residue in the boat has the appearance of a dark, black, coherent mass. When brought into water, this black residue slowly gives off a gas. If now a drop or two of a solution of ammonium chloride be added, a moderately rapid current of gas is given off. This gas has an odour like that of acetylene, but when it is conducted through an ammoniacal solution of cuprous chloride, the greenish yellow precipitate of cuprous ally-

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* Imperial Academy of Science at Vienna, February 7, 1895.

* Read at the Chemical Section of the Franklin Institute, Dec. 18, 1894.

lide is formed. In an ammoniacal solution of silver nitrate, a white crystalline precipitate of silver allylide is obtained. Both these precipitates, when they are filtered off, washed, and dried, explode if they are heated up to about 150°. When treated with dilute nitric or hydrochloric acids, they dissolve with an evolution of allylene. The silver precipitate can be obtained in pure condition more readily than the copper compound. An analysis of the former gave the following result:—

I. 0·1292 grm. gave 0·1270 grm. AgCl = 73·97 p. c. Ag.
Calculated for C_3H_3Ag, 73·45 „ „

The gas which was given off during the time that the magnesium in the porcelain boat was glowing in the methyl alcohol vapour, gave, on analysis, the following results:—

CO_2	0·8
CO	0·6
CH_4	19·7
H	78·9
	100·0

The action of zinc dust upon the vapour of methyl alcohol has been examined by W. Jahn (*Monatshefte*, 1880, i., 378 and 675), who found that the chief products were hydrogen and carbon monoxide. As a by-product, a small quantity of marsh gas was obtained. It is evident, from the above analysis, that the action of the magnesium is essentally different, the carbon monoxide being practically absent in the products obtained when this metal acts upon the methyl alcohol. We have found that another metal, namely iron, decomposed the methyl alcohol vapour in the same way that zinc does. Thus, when the methyl alcohol vapour was passed through a tube containing iron, as, for example, a boat made of thin iron sheet, the alcohol was decomposed into carbon monoxide and hydrogen. An analysis of the gas thus obtained gave the following results:—

CO_2	3·8
CO	26·8
CH_4	1·6
H	67·4
	99·6

In short, when methyl alcohol is passed over heated metals, such as iron or zinc, it is resolved into hydrogen and carbon monoxide; if it be passed over heated magnesium, the chief products are hydrogen and marsh gas.

The next alcohol examined was ethyl alcohol. The action in this case was similar to that described in the case of methyl alcohol. The residue remaining in the boat was treated with water and a few drops of ammonium chloride solution, and the gas that was given off was conducted through a series of bottles containing an ammoniacal solution of silver nitrate. The white crystalline precipitate, on analysis, gave the following percentage of silver:—

I. 0·1163 grm. gave 0·11365 grm. AgCl = 73·53 p. c. Ag.
II. 0·0979 „ 0·09615 „ „ 73·89 „ „
Calculated for C_3H_3Ag, 73·45 „ „

In this case, also, allylene is given off when the magnesium residue is decomposed by water. The gases formed during the action have the following composition:—

CO_2	0·0
CO	0·4
C_2H_2	10·0
C_2H_4	4·0
CH_4	11·1
H	72·9
	98·4

The chief constituent again is hydrogen. Carbon monoxide is practically absent, as we should expect, knowing that this gas is reduced by magnesium. Acetylene and marsh gas are present in about equal quantities. Jahn found that zinc dust at low temperatures decomposes ethyl alcohol smoothly into ethylene and water, the latter being reduced to hydrogen by the zinc. At higher temperatures he obtained hydrogen, marsh gas and carbon monoxide, and a trace of acetylene. We have found that iron decomposes ethyl alcohol in very much the same way that zinc does at elevated temperatures. The gas obtained by passing ethyl alcohol over heated iron had the following composition:—

	CO_2	0·5
	CO	8·0
Unsaturated hydrocarbons	$C_2H_2+C_2H_4$	4·0
	CH_4	13·0
	H	63·8
		99·3

Propyl alcohol was examined in the same way. In this case the black magnesium residue is decomposed by water at the ordinary temperature, and the quantity of silver precipitate is very much greater than in the preceding cases. So readily is allylene obtained from propyl alcohol and magnesium by this method, that for the purpose of preparing the gas for experiments on the lecture table it is much to be preferred to the ordinary method of decomposing propylene bromide with alcoholic potash. Analysis of the pure white silver allylide thrown down in the second wash-bottle from the generating flask gave, on analysis, 73·39 per cent of silver.

0·15605 grm. gave 0·1522 grm. AgCl = 73·39 per cent Ag.
Calculated for C_3H_3Ag = 73·45 „

The precipitate in the first wash-bottle was not so pure; it evidently contained some silver acetylide. On analysis, 0·20095 grm. gave 0·19985 grm. AgCl, or 74·83 per cent. Silver acetylide contains a higher percentage, namely 89·99 per cent of silver.

An analysis of the gases formed when the magnesium acts upon propyl alcohol showed that in general the action is similar to that which took place in the experiments with ethyl alcohol. The analysis gave these figures:—

CO_2	0·0
CO	3·5
Unsaturated hydrocarbons	17·8
Saturated „	19·9
H	57·8
	99·0

The chief products of the decomposition of propyl alcohol, under the action of magnesium, are hydrogen and saturated and unsaturated hydrocarbons, the latter being present in nearly equal volumes. The same alcohol is decomposed by heated iron in a different way, the analysis of the gas having given the following values:—

CO_2	0·6
CO	16·4
Unsaturated hydrocarbons	16·7
Saturated „	23·6
Hydrogen	42·7
	100·0

With zinc dust Jahn found that, at low temperatures, propylene and hydrogen are the chief products.

The other alcohols that have been examined are allyl, isobutyl, and amyl alcohols. The first of these, namely, allyl alcohol, is even better than normal propyl alcohol for the preparation of allylene. An abundant precipitate of silver allylide is obtained, and an analysis showed that it was free from silver acetylide.

I. 0·17185 grm. gave 0·16735 grm. $AgCl$ = 73·27 p.c. Ag.
Calculated for C_3H_3Ag = 73·45 „

In this case the precipitate obtained in the first wash-bottle gave on analysis a result which showed that it contained no silver acetylide.

0·16705 grm. gave 0·1620 grm. $AgCl$ = 72·97 per cent Ag.
For C_3H_3Ag = 73·45 „

The ease with which, from a few c.c. of propyl or allyl alcohols and a few grms. of magnesium powder, an appreciable quantity of allylene silver can be obtained, makes this method of preparing allylene much more convenient than the one ordinarily used.

From isobutyl alcohol and magnesium a residue was obtained, which, on treatment with water and ammonium chloride, gave a gas which, besides hydrogen, contained acetylene and allylene, as was shown by the percentage of silver in the silver precipitate.

0·18335 grm. gave 0·18845 grm. $AgCl$=77·33 per cent Ag.

From amyl alcohol the yield of silver precipitate was not very large, but here also the unsaturated hydrocarbon was allylene.

0·08585 grm. gave 0·08365 $AgCl$=73·31 per cent Ag.

Other alcohols and organic compounds containing oxygen will be investigated in a similar way.

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.*

By AMOS PEASLEE BROWN.

While much has been done in the way of investigating the chemical properties and constitution of the various artificial chemical compounds, comparatively little attention has been paid to the constitution of the naturally occurring chemical compounds. The carbon compounds, for instance, have in an immense number of cases been investigated with sufficient exactness to allow of our expressing their constitution by means of structural formulæ, but to how many minerals, aside from the simplest compounds, can we assign structural formulæ that are based on any knowledge that we possess of their reactions? It is true that much has been done in the way of the artificial production of minerals, and some knowledge of the constitution of certain minerals has been arrived at by a study of their decomposition products, but very little in comparison to the extent of the field. There are probably several reasons for this neglect of the study of the chemical properties and constitution of minerals, as want of homogeneity in the minerals themselves, difficulty of procuring or separating pure material for investigation, and similar difficulties which do not so frequently occur with artificial compounds. It thus happens that mineral chemistry is not as much studied as it deserves to be. Certain groups of minerals have, however, received some attention; for instance, Professor F. W. Clarke has been carrying on a very interesting series of investigations on the constitution of certain silicates which have been productive of most valuable results. The natural sulphides, sulpharsenides, and sulpho-salts present some very interesting problems in regard to their constitutton, and it was with a view of adding to our knowledge of the chemical behaviour of two of these sulphides that I undertook the series of investigations about to be described.

The compound FeS_2 is found in nature in two well-known forms—the one pyrite (the isometric mineral) and the other marcasite (the orthorhombic mineral). Since the separation of the two names from the general term, pyrites, it has been recognised that the orthorhombic form is lighter in colour and also of lower specific gravity than the isometric form. From early times, also, the greater tendency of "white pyrites," or marcasite, to decompose in the air was well known.

Pyrite, the form which resists atmospheric weathering most thoroughly, is of a bright brass-yellow colour and metallic lustre, breaking with an uneven conchoidal fracture, but bright on the surface of fracture. It crystallises in the isometric system in forms showing generally pentagonal hemihedrism. Its specific gravity ranges from 4·8 to 5·2, averaging somewhat over 5. The brass-yellow crystals are generally quite unaltered in the air.

Marcasite, on the other hand, has a pale greenish or greyish yellow colour, an uneven fracture, which shows a somewhat fibrous structure, and generally but little lustre on the surface of fracture. It crystallises in the orthorhombic system, very commonly in twins or radiated fibrous masses. It is not very permanent in moist air, but readily decomposes and largely into $FeSO_4$. The chemical formula of either form, calculated from quantitative analyses, is the same, FeS_2 or Fe=46·67 per cent, S=53·33 per cent.

The chemical study of these two minerals has been mainly confined to the formation of one of them artificially and to a few experiments on their relative decomposability. Pyrite has been made artificially in a number of ways; marcasite has not as yet been formed artificially. (Doelter, *Zeit. fur Kryst.*, xi. 31, 1885; cf. Dana, "Syst. Min.," 1892). In 1836, Wöhler (*Pogg. Ann.*, xxxvii., p. 238) produced cubes and octahedra of pyrite by subjecting a mixture of ferric oxide, flowers of sulphur, and ammonium chloride to a temperature a little above the volatilising point of the ammonium chloride. The resulting mass was washed to isolate the crystals from the accompanying pulverulent matter. Stanislas Meunier ("Les Méthodes de Synthése en Mineralogie, S. Meunier, 1891") modified this method by mixing equal parts of ferrous carbonate and sulphur and heating in glass tubes over a moderate flame. When the excess of sulphur has been driven off, there remains a black powder containing a considerable percentage of cubes of pyrite. Dana ("System of Mineralogy," edition of 1868, p. 64) states that pyrite may be made "by slow reduction of ferrous sulphate in presence of some carbonate." Baubigny (S. Meunier, "Synth. Min.," p. 279) produced FeS_2 as a crystalline crust by acting on metallic iron by a solution of SO_2 in water (H_2SO_3) in closed tubes and at a temperature of 200°. As neither this experiment nor the one immediately preceding it shows that the crystals were isometric, it is possible that both of them may be marcasite. Henri Sainte Claire Deville (cited in "Dict. Chem." of Wurtz, by E. Wilm, article "Iron," i., p. 1414) produced cubes of pyrite by melting a mixture of potassium sulphide (K_2S) and iron sulphide (FeS) in presence of excess of sulphur. This reaction, if correct as to the *cubical* product, is a remarkable one, as I should rather expect marcasite to result under such conditions. Senarmont (S. Meunier, "Synth. Min.," p. 285) produced FeS_2 by decomposing a salt of iron by an alkaline sulphide at an elevated temperature in sealed glass tubes. The product was an amorphous black powder, not altering on exposure to air and not attacked by hydrochloric acid. This may have been pyrite, as marcasite is readily decomposed by moist air. Rammelsberg (*Jour. fur Praktische Chemie*, lxxxviii., p. 266), in 1862, made FeS_2 pseudomorphs after ferric oxide (Fe_2O_3) by passing a current of hydrogen sulphide over it at a temperature between 100° and a red heat. The product of this reaction would likely be pyrite.

In nature it would seem that in most cases the sulphide of iron first formed is FeS, but probably by action of a ferric salt, or carbonic acid (H_2CO_3), causing a loss in iron, FeS_2 results, and this is almost always pyrite. On the other hand, where ferrous sulphate has been reduced by slow action of decomposing organic matter, the resulting sulphide seems to be generally marcasite, which

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* Read before the American Philosophical Society, May 18, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

if not in crystals may be recognised by its ready weathering to ferrous sulphate ($FeSO_4$). This compound may, however, in many cases, be a mixture of pyrite and marcasite, as much pyrite seems to be. (Compare A. A. Julien, "Decomposition of Pyrite," *Ann. N. Y. Acad. Sci.*, iii. and iv.). These several ways in which pyrite may be formed are of importance as indicating the condition of the iron in the compound, and will be referred to later on.

Equally important as bearing on the constitution of these sulphides are the observations that have been made as to their decomposition under atmospheric agencies. On exposing crystallised pyrite to atmospheric weathering it is generally found that but little, if any, change takes place even in a year's time, while crystallised marcasite, under the same conditions, shows a rapid weathering. The main product of the weathering of pyrite in nature is the compound limonite, $Fe_4O_3(OH)_6$, which occurs in large quantities in nature, evidently derived from pyrite. Its pseudomorphs after pyrite are very common. On the other hand, when marcasite weathers a very large percentage of ferrous sulphate ($FeSO_4$) is formed with a comparatively small percentage of limonite, unless the marcasite decomposes underground and under pressure, when limonite is largely produced (Blum, "Pseudomorphosen," 1843, pp. 197—199). Much of the excess of sulphur with marcasite is changed to sulphuric acid, but with pyrite much remains behind as sulphur. Some comparison of the rate of oxidation of these two minerals in the air is afforded by an examination of specimens in a collection. Here it will be found that most of the pyrite is unchanged, but nearly every specimen of marcasite will show tarnish if no other sign of oxidation, and often a considerable coating of oxide can be seen, or a white efflorescence of $FeSO_4$.

Chemical investigations of these two minerals have been mainly in the way of analysis, but some experiments have been made in the way of studying their relative behaviour towards certain reagents. Before describing my experiments, it will be necessary to briefly mention some of these.

Both minerals are decomposed by a solution of silver nitrate and gold chloride, the decomposition taking place quite rapidly (S. Meunier, "Synth. Min." p. 309). My experiments in this connection are mentioned later.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 21st, 1895.

Dr. Armstrong, President, in the Chair.

Mr. Alexander Cameron was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Herbert William Cook, B.Sc., West Mount, Upton, Macclesfield; Edric Druce, Worleston, Nantwich; H. Loft Haller, 27, Hilda Street, Beverley Road, Hull; George Elliott Shaw, 9, Basing Road, Westbourne Park, W.

It was announced that the following changes in the Officers and Council were proposed by the Council.

As *President*—A. G. Vernon Harcourt, M.A., D.C.L., LL.D., F.R.S., *vice* Professor H. E. Armstrong, LL.D., Ph.D., F.R.S.

As *Vice-Presidents*—Professor Roberts-Austen, F.R.S., and Professor Japp, F.R.S., *vice* A. Vernon Harcourt, F.R.S., and Professor William Ramsay, F.R.S.

As *Ordinary Members of the Council*—Professor Bedson, Mr. B. Brough, Mr. Hehner, and Professor McLeod, F.R.S., *vice* Charles F. Cross, A. G. Green, W. H. Perkin, jun., F.R.S., and John A. Voelcker, Ph.D.

Messrs. Evan Bevan, Bertram Blount, and E. W. Voelcker were appointed to audit the Society's accounts.

The following were duly elected Fellows of the Society:—Herbert Anderson, John Melrose Arnot, David Butler Butler, Francis H. Carr, Thomas Bennett Case, B.A., Tom Crossman, Frederic Weldon Daw, Edward Elliott, Henry Fairrie, Alexander Macfarlane, Herbert Edward Gardner, Henry Tresawna Gerrans, M.A., George Goldfinch, Donald St. John Grant, M.A., M.B., Herbert Grime, Weldon Hanson, Harry Harris, Walter Harris, B.A., Ph.D., Hugh Hastings, John Adams Hatfield, Edward Herbert Hill, Percy Hudson, Edgar Joseph, Richard Ernest Kenyon, B.Sc., George Holman Kingdon, B.A., Patrick Henry Kirkaldy, Arthur Marshall, William Baxter McVey, Robert Meldrum, Harry Edward Niblett, B.A., James Albert Offord, Harry James Powell, Herbert Lewin Robinson, Thomas Chilwell Sharrot, Herbert Frederick Stephenson, Henry R. Le Sueur, B.Sc., Thomas C. Warrington, B.A., David John Williams, Evan Williams, Harry Wilson, Henry Stow Young.

Of the following papers those marked * were read:—

*20. "*The Electromotive Force of an Iodine Cell.*" By A. P. Laurie, M.A.

A cell consisting of a zinc and platinum plate, immersed in a solution of iodine in potassium iodide, gives a definite and constant E.M.F., the zinc being dissolved at the expense of the iodine surrounding the platinum plate. On diminishing the strength of the iodine solution the E.M.F. gradually falls off, the rate increasing as the iodine becomes very dilute; the E.M.F. for a 0·1 per cent solution being 1·460 volts, and for a 0·001 per cent solution 1·369 volts. If potassium iodide free from iodine is used, an E.M.F. of about 1·172 volts is obtained. This value is uncertain, and varies for different platinum wires and at different times for the same platinum wire, the highest value being obtained with a wire boiled in soda, then in nitric acid, then washed, and finally heated white-hot. If this wire, however, is left in the solution it gradually falls in E.M.F. to about the value given above.

On adding a trace of iodine, 0·0001 per cent, the E.M.F. at once rises to about 1·320 volts, the reading differing slightly for different wires, and on increasing the amount of iodine the E.M.F. goes on rising, the readings rapidly approximating until before 0·001 per cent is reached the readings are all the same.

Above this value the E.M.F. rises more slowly, but with regular movements; consequently the E.M.F. becomes a measure of the strength of the solution. The author proposes to use these results for measuring the rate of diffusion of very dilute solutions of iodine, and has made more preliminary experiments with the view of doing this.

On diffusing a solution of 0·01 per cent iodine from a short glass tube, with a platinum wire inserted in the closed end, into a mixture of potassium iodide, and taking readings of E.M.F. every half hour, a very regular curve was obtained showing the gradual diminution of the strength of the iodine solution, and in substituting cadmium for potassium iodide as the solvent, results were obtained so nearly agreeing that apparently the iodine is diffusing independently of the potassium iodide or cadmium iodide molecules. The author is now engaged in trying to measure the actual rate of diffusion, and the relation between the rate of diffusion and the temperature of the solution. Incidentally the results show that determinations of the E.M.F. between metals and solutions require in certain cases to be made with considerable care, if the results are to be of any value.

*21. "*Contributions to the Chemistry of Cellulose.*" By C. F. Cross, B.Sc., E. J. Bevan, and C. Beadle.

In a recent monograph ("Cellulose," Longmans, 1895) the authors have suggested a classification of the experimental facts on this subject, and at the same time have pointed out directions for future research. The present paper is a report of progress of investigation upon these lines. The first part is devoted to generally tracing the analogies of cellulose, as a chemical unit, with the salts, and incidentally the points of sharp distinction between cellulose and starch ; the experimental study of these points leads to the conclusion that it is not a polyaldose (or aldosan) of the starch type. The points emphasised are :—1. The resistance to hydrolysis as exemplified by the quantitative regeneration of cellulose from the cycle of reaction involved in the formation and decomposition of the xanthates. 2. "Double salt" reactions of cellulose with zinc salts, and the interaction of the cellulose-zinc acetate with acetyl chloride in the cold (at about 30°) forming acetylated derivatives. 3. The mode of decomposition of these cellulose acetates points to the formula $C_6H_6O(OAc)_4$. 4. Certain electrolytic phenomena of the cellulose hydrates which show that in presence of water cellulose is sensitive to the action of the electric current; the metal of a metallic conductor, taken as the "positive" or anode, is attacked and carried forward in the direction of the current, and deposited in the cellulose in a condition of chemical union.

These points have been worked out in experimental detail, and establish several characteristic features which sharply distinguish it from other "colloidal carbohydrates." The electrolytic phenomena are, however, shown by very various substances, *e.g.*, silk, wool, asbestos, &c. In the later sections of the paper the authors, in collaboration with Claude Smith, give the results of experiments on the special group of "natural oxycelluloses," of which the celluloses of the *Gramineæ* are typical. These researches include (1) studies of germination in relation to the furfural-yielding constituents of the tissues of the seedlings; (2) the further history of the plant, for which special barley plots of the Woburn experimental station were selected. The authors have also investigated the furfural reaction, and determined the proportion of volatile acids (formic and acetic) which are formed as bye-products of the condensation. Progress has likewise been made in isolating the "furfuroids" of these celluloses. Treatment with sulphuric acid of 1·6 specific gravity and dilution with water separates the fibrous cellulose into a normal cellulose (insoluble hydrate) and soluble carbohydrates giving a large yield of furfural (50 per cent), but none of the characteristic reactions of the pentosans. It appears to be now generally admitted that these furfural-yielding constituents of plants are products of metabolism of hexoses and hexosans (Cross and Bevan, *Berl. Ber.*, xxvi., 2520 ; xxvii., 1061 ; De Chalmot, *ibid.*, xxvii., 1489), though the question of their identity seems to be still a matter of controversy. The evidence, however, so far is against an indiscriminate classification of these bodies as pentoses and pentosans.

*22. "*The Melting-points of Mixtures.*" By Holland Crompton and Miss M. A. Whiteley.

The authors have determined the melting-points of mixtures containing two organic compounds in various proportions. They come to the following conclusions from the results of these experiments :—

1. In all normal cases of solutions in which on solidification the solvent first of all separates out in the pure state, the relationship—

$$\log s = \frac{\rho}{1{\cdot}98} \cdot \frac{T - T'}{TT'}$$

holds. Here *s* is the number of molecules of the solvent contained in one molecule of the solution, ρ is the molecular latent heat of fusion, and T the melting-point in absolute temperature of the solvent, T' the melting-point of the mixture or solution.

2. For ρ, the value $1{\cdot}38\ \Sigma vT$ can be substituted where Σv is a number derived from the valencies of the atoms comprising the molecule (*Proc.*, 1894, 240).

3. In a number of instances the observed melting-points of the mixtures are higher than those calculated by these formulæ, and in such cases the discrepancies may be accounted for by assuming that the pure solvent does not separate out from the solution on solidification, but that a solid solution is formed by union of a certain quantity of the dissolved substance with the solvent.

*23. "*The Volumetric Determination of Manganese.*" By Joseph Reddrop and Hugh Ramage.

The authors have examined a method proposed by L. Schneider (*Journ. Chem. Ind.*, 1888, p. 693), in which the manganese salt is oxidised by bismuth peroxide in presence of nitric acid to permanganic acid. After filtration through asbestos, the permanganic acid is determined by titration with hydrogen peroxide. The best strength of nitric acid is 250 c.c. (sp. gr. 1·2) per litre, but the permanganic acid decomposes in the acid solution, and to prevent this decomposition it is filtered into an excess of hydrogen peroxide, and finally titrated with potassium permanganate. It is shown that the error in Schneider's method is at least 0·6 per cent in the analysis of ferromanganese, and 0·06 per cent in that of steel.

Sodium bismuthate prepared from materials free from chlorine, replaces the bismuth peroxide used by Schneider. It is prepared by fusing soda, basic bismuth nitrate, and sodium peroxide ; on washing with water the insoluble compound remains.

The analysis of ferromanganese, spiegel, silico-spiegel, iron, and steel are described in detail, and the accuracy of the method established by experiments on quantities of manganese ranging from 0·1 per cent to 80·7 per cent. In a sample of ferromanganese, they obtained by the ordinary gravimetric method, using ammonium salts and correcting for impurities, 80·63 per cent ; by Pattinson's method, 80·70 per cent ; by the present method, 80·67 per cent. Chromium, copper, nickel, and cobalt up to 5 per cent, are shown to raise the results but very slightly. Sulphuric acid up to normal strength does not interfere, and may therefore be used to expel hydrochloric acid from solutions in which it has been used in dissolving the sample.

The oxidation, filtration, and titration may by this method be completed within fifteen minutes.

24. "*Bromocamphoric Acid, an Oxidation Product of π-Dibromocamphor.*" By F. Stanley Kipping, Ph.D., D.Sc.

It has recently been shown (Kipping and Pope, *Proc.*, 143, 212) that an optically active π-dibromocamphor, melting at 152—153°, can be prepared by gently heating bromocamphorsulphonic bromide ; the further investigation of this dibromo-camphor has already led to interesting results, which are briefly described in this note.

On boiling the π-dibromo-compound with concentrated nitric acid for some hours a part undergoes oxidation, and on cooling and adding water a crystalline product is deposited, together with a pale yellow thick oil.

The crystalline product separates from alcohol in nodular aggregates, and melts at about 217° with decomposition ; its melting-point and its origin seemed to point to its identity with the bromocamphoric anhydride (m. p. 215—216°) described by Wreden, and more recently investigated by Rupe and Maull, Auwers and Schnell, and Aschan, but analysis and further examination showed that this was not so. The compound has the composition $C_{10}H_{15}BrO_4$ (found C=43·2, H=5·4 ; Calc. C=43·0, H=5·4 per cent) ; it has an acid reaction to litmus, dissolves freely in cold sodium carbonate solution, and also differs from bromocamphoric anhydride in being only very sparingly soluble in chloroform. For these and other reasons it must be regarded as a *bromocamphoric acid*, structurally isomeric with the as yet unknown bromocamphoric acid from which Wreden's anhydride is derived.

When the acid is gently heated with acetic chloride it is converted into the anhydride $C_{10}H_{13}BrO_3$ (found C=45·92, H=5·16 ; Calc. C=45·97, H=4·97 per cent) ; this compound crystallises very well, melts at 155—156°, and does not dissolve in cold sodium carbonate solution.

When the acid is warmed with aqueous potash for a few minutes and the solution cooled, no precipitate is produced on acidifying (although the original acid is very sparingly soluble in cold water); alcoholic potash also acts readily on the acid, converting it into a very thick colourless syrup, which could not be crystallised. This syrup has an acid reaction, is miscible with water, and dissolves in aqueous sodium carbonate with effervescence, giving a solution which does not reduce potassium permanganate; it seems to be a hydroxy-acid of the composition $C_{10}H_{16}O_5$ (found $C=54{\cdot}2$, $H=7{\cdot}4$, Calc. $C=55{\cdot}5$, $H=7{\cdot}4$), but as it was not specially purified the analysis is not decisive.

The pale yellow oil which is obtained along with the bromocamphoric acid is a mixture; when it is warmed with alcoholic potash for some time, and the alcohol evaporated crystals of the original π-dibromocamphor are deposited, and the alkaline solution yields when acidified a crystalline substance which contains nitrogen. This is a *nitrobromocamphor*, $C_{10}H_{14}(NO_2)BrO$ (found $C=43{\cdot}21$, $H=5{\cdot}07$), but is not identical with the known compound; it separates from a mixture of chloroform and light petroleum in needles melting at 133—134°, and is soluble in aqueous potash and sodium carbonate, but is almost insoluble in water.

25. "*Note on the Action of Diastase on Cold Starch-Paste.*" By Horace T. Brown, F.R.S., and G. Harris Morris, Ph. D.

The authors draw attention to the generalisation which they claim to have established in previous communications, namely, that the products of a starch transformation, or any part of them separated by any method of fractionation, can always be expressed, in the terms of maltose, having an optical activity $[\alpha]_{j3\cdot86}=150°$, and a cupric-reducing power of $\kappa_{3\cdot86}=61$, and of dextrin, having an optical activity of $[\alpha]_{j3\,86}=216°$ and no reducing power; in other words, knowing the cupric-reducing power of any starch product, the optical activity can be predicted with accuracy, and *vice versa*. This fact is quite independent of any consideration of the true nature of the intermediate products between starch and maltose, and has been ignored by certain recent workers.

In a paper by Brown and Heron (*Trans.*, 1879, p. 627) it is mentioned that during the early stages of the action of diastase upon starch-paste in the cold, there is an apparent exception to this rule, the optical activity being *lower* than it should be on the assumption that only maltose and dextrin are present. After standing some hours, or on boiling, this discrepancy disappears, and the optical cupric reducing powers show the same relationship that they do in conversions made at higher temperatures. An observation made by O'Sullivan and Tompson in another direction suggested an explanation of these abnormal results, and in the present paper the authors show that the lower angle of rotation observed during the earlier stages is due to the maltose being liberated in the state of "half rotation," a condition which freshly-prepared solutions of pure maltose always show. When freshly dissolved the optical power of maltose bears the relation to that of a boiled or old solution of about 133° to 150°, and the authors show that this relationship holds good in the case of freshly-prepared products from cold starch-paste.

26. "*On the Magnetic Rotation of some Unsaturated Hydrocarbons.*" By W. H. Perkin, Ph.D., F.R.S.

In this paper it is shown that the magnetic rotations of the olefines do not differ from those of the paraffins to quite such a large extent as do other substances correspondingly unsaturated, the vinyl compounds excepted. In the case of diallyl, which is twice as unsaturated, the increase in the magnetic rotation is, however, proportionally a little larger, being more than twice that of the olefines. A comparison is made of the boiling-points, densities, and specific rotations of the six carbon hydrocarbons, hexane, hexylene, diallyl, and dipropargyl, and it is shown that the differences between dipropargyl and diallyl are not of the same order as of those between hexane and hexylene, being of an opposite kind in the boiling-points and much larger in the other properties. The molecular rotations, however, which involve both density and specific rotation, exhibit greater regularity, the two acetylene linkages influencing the molecular rotation to the same extent as four ethylene linkages. The molecular rotation of isoprene does not differ much from that of diallyl, if the difference of CH_2 in its composition is allowed for.

List of Fellows.

A new List of Officers and Fellows of the Chemical Society being in course of preparation, it is requested that Fellows will send any alteration of Name or Address, without delay, to the Assistant-Secretary, Burlington House, London, W.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, March 4, 1895.

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 Grace the Duke of Newcastle, Lieut.-Col. W. W. Rawes, R.A., Dr. Marmaduke Prickett, Miss C. E. Bradshaw, Mrs. Alexander Goschen, and Messrs. G. S. Albright, E. G. Betts, R. A. Bray, M. Bulloch, G. Bywaters, G. F. N. Clay, C. S. Dickson, J. J. Elliott, J. Garvie, F. L. Harris, E. G. Harrison, S. C. Hogg, E. Law, G. H. Ogston, B. P. Portal, S. J. Portal, W. T. Shaw, J. H. Skelton, J. J. Walker, W. H. Walker, and A. F. Walter.

The Special Thanks of the Members were returned to Sir William J. Farrer and Mr. John Douglas Fletcher for their donations to the Fund for the Promotion of Experimental Research at Low Temperatures, and to Mr. Hugh Spottiswoode for a portrait of his father, the late Mr. William Spottiswoode.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Dr. Dobbin in the Chair.

The seventh meeting for this Session was held on February 26.

A paper was read by Mr. Alexander Lauder on the "*Fixation of Atmospheric Nitrogen.*"

The paper gave an account of the more important of the different attempts which have been made to utilise the nitrogen of the atmosphere for the preparation of ammonia or potassium cyanide. A description of the process of preparing potassium ferrocyanide from refuse, organic matter, iron, and potassium carbonate was first given, Liebig's theory of the process being briefly discussed. The more important of the various processes proposed for the fixation of atmospheric nitrogen were then considered in historical order.

Attention was first directed to this subject by the discovery of masses of a fused salt at different iron furnaces, which analysis showed to contain a large percentage of potassium cyanide. The source of the nitrogen contained in the potassium cyanide was the subject of active discussion, until accurately conducted laboratory experiments proved that nitrogen is capable of combining with carbon and potassium to form potassium cyanide. Carefully purified nitrogen was passed over a mixture of pure carbon and potassium hydrate, heated in a tube to bright redness, and potassium cyanide was found in the residue. A short account was given of the famous investigation carried out in 1845 by Bunsen and Playfair on a blast furnace at Alfreton which produced potassium cyanide. They came to the conclusion that potassium cyanide was only formed at the temperature at which potassium oxide gives up its oxygen to carbon, and that the conditions favourable to the production of cyanides were a reducing atmosphere and a temperature of the degree already mentioned.

The following was the average composition of the gas drawn from the furnace through a hole made in the front wall about 2 ft. 9 in. above the blast pipes:—

Nitrogen .. .. .. = 58·05 per cent.
Hydrogen . .. .. = 3·18 „
Carbonic oxide .. = 37·43 „
Cyanogen . .. .. = 1·34 „

After the possibility of direct combination of nitrogen with carbon and potassium had been proved, attempts were immediately made to apply the principle to manufacturing purposes on the large scale. Many patents were taken out for this purpose, but the majority of them were quite unsuccessful. The process of Possoz and Boissiere,* carried on first at Grenelle, near Paris, and latterly at Newcastle-upon-Tyne, was considered in some detail. In this process the atmospheric air was first passed through a coal fire to convert the oxygen into oxides of carbon; the mixed gases next passed through white-hot flues to large cylinders of fire-clay charged with charcoal saturated with potassium hydrate, and which were also kept at a white-heat. The process worked continuously, the cyanised charcoal being drawn off at the bottom, and more alkaline charcoal fed in at the top. The works were continued for three years (1844 to 1847), and were then abandoned after considerable loss. The cause of failure was principally due to the rapid destruction of the retorts by the potash at the high temperature necessary to carry out the reaction.

Other processes, in which baryta was used as the base instead of potassium hydrate, were also considered. The paper concluded with a short discussion of the various conditions which experience has shown to affect the process, *e.g.*, the temperature at which the reaction is carried out, the action of the base which is always present, the most suitable base to use, and the influence of water vapour and of oxygen on the reaction.

NOTICES OF BOOKS.

Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics. By Prof. WALTER NERNST, Ph.D. (of the University of Göttingen). Translated by Prof. CHARLES SKEELO PALMER, Ph.D. (of the University of Colorado). With Twenty-six Woodcuts and Two Appendices. 8vo., pp. 697. London and New York: Macmillan and Co. 1895.

IN noticing a work of this kind we have to consider not only the author, but the translator. That Prof. Palmer thoroughly understands and appreciates Prof. Nernst cannot be questioned. But whether the former has always succeeded in making "the sound German speak good English" is sometimes doubtful. Thus whether or no the expression "Waermetönung" was the happiest possible, it is undeniably good German. But "heat-toning," here used as its equivalent, cannot be regarded as good English. Prof. Palmer repeatedly uses "knall-gas" as a translation of the German Knall-gas where we should say "detoning-gas." The misfortune is that any Englishman, except he has been educated in Germany, will pronounce the word "nall-gas." "Schlieren" is a word which cannot be tolerated in an English work; "layers" or "strata" would express the author's meaning with sufficient clearness. As to minor peculiarities in expression and orthography, we cannot expend time and space in their mention.

The work itself is one which deserves the most hearty recommendation. Advanced students will find it an invaluable guide to chemical theory in its present stage of development. After an introduction which will be profitable reading even for the experienced chemist, especially if he understands German, the author undertakes an examination of the universal properties of matter, of the atom and the molecule, of the transformation of matter, and the transformation of energy. These last two books deal very fully with the doctrine of affinity, which, as here pointed out, is originally a biological conception. We must here add that, whilst scarcely satisfied of Prof. Palmer's competence to render a foreign work into English, we have the highest opinion of his merits as a chemical philosopher. The footnotes which he has added greatly enhance the value of the work—*e.g.*, those on pp. 354, 355, 431, &c.

Prof. Nernst, as well as his translator, is far from undervaluing the hypothesis of Avogadro. On the capital but unsolved question whether our reputed elements are anything beyond the present limit of our analytical resources, neither of these authorities pronounces a decided opinion. Prout's hypothesis is definitely rejected (Appendix 1, p. 629), in accordance with the researches of Landolt. It is, however, clear that the near approach to the values which Prout's hypothesis would require is not accounted for.

On p. 296 the author mentions the law discovered by Nietzki, *i.e.*, that the simplest colouring substances are in the greenish-yellow and yellow, and with increasing molecular weight the colour passes into orange, red, violet, blue, and green. This law involves some interesting corollaries which cannot be touched upon in a notice of Prof. Nernst's work. The remark of Schütze is also here quoted, that in analogous elements an increase of atomic weight involves deepening of the colour.

In discussing solid solutions—*i.e.*, the solution of one solid in another—the author refers to the view of Witz, that the process of dyeing consists in the solution of the pigment in the fibre. Thus the dyed fibre does not show the colour of the solid colouring-matter, but of its solutions,—*e.g.*, the cases of magenta, rhodamine, &c. The theory of indicators is explained as according to Prof. Gladstone, Salet, Magnanini, and others.

In controversies Prof. Nernst does not always observe the *leniter in modo.* Thus he refers to Berthelot's "usual offensive style" (p. 585). This is to be regretted.

Appendix II., containing a "synchronistic comparison of the most important chemical journals and allied periodicals," suggests various reflections. We notice, firstly, how far the German journals outnumber those of France, England, and America, taken conjointly. Secondly, we are again impressed with the difficulty of keeping in view the world's entire work in chemistry. Now Memoirs are appearing in Rumanian, Czech, Servian, Polish, and Russian, the task becomes practically impossible. Who can suggest a remedy? The proposal made that whatever is not published in German, French, or English, shall be regarded as unpublished, even if accepted, would not fully meet the difficulty.

It will not be considered a vain repetition if we once again recommend Prof. Nernst's work to students, not as something to be examined in, but to be comprehended and assimilated.

The Specialist's Series. Steel Works Analysis. By J. O. ARNOLD, F.C.S., Professor of Metallurgy at the Sheffield Technical School, some time Chief Chemist at the Sheffield Steel and Iron Works. Crown 8vo., pp. 350. London: Whittaker and Co., 2, White Hart Street, Paternoster Square. New York: 66, Fifth Avenue. 1895.

THIS book possesses some very good features, which unfortunately are not in all cases to be found in chemical annuals. The author does not present us with a com-

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* See article on "The Fixation of Atmospheric Nitrogen," by Prof. Breneman, CHEMICAL NEWS, 1890.

pilation, but writes from his own experience. Doubtful processes are judiciously left aside, the student or the young expert being thus not bewildered with the choice between methods. He protests against the "appalling elaboration" with which authors on the chemistry of iron and steel discuss the separation of elements possible, but very rare.

A remarkable but not useless feature in this work is the statement of the time whicn each process may be expected to require. We find the remark that, if certain procedures were adopted, "the world would have to wait for its iron." We are here reminded of the utterance of a thinker who represents Nature saying to Man — "Why all this hurry, my little Sir?"

There is a useful list of the materials upon which a steel works' chemist must be prepared to report. Mr. Arnold appends to most of his directions an abstract of the theoretical considerations involved. This course has been adopted because he has found the knowledge of pure chemistry possessed by pupils and junior asistants less than what is commonly and reasonably expected.

At the end of the book we find a list of normal compositions of the substances most commonly encountered by the steel-works' chemist. There is a table of atomic weights, in which we regret to find platinum still figuring higher than gold. There is the *banal* denunciation of English weights, though the decimal system would long ago have been taken into use had it not been encumbered with its present Græco-Latin nomenclature.. Hydrometer scales, in which we have a distinct advantage over our Continental neighbours, are not mentioned.

After considering the apparatus and the manipulations necessary, the author gives in succession instructions for the analysis of the metals and alloys which come under the hands of the steel-works' analyst; of the ores of iron, manganese, chrome, tungsten; of refractory materials, fuels, slags, and boiler-water. Under the last head, of course, many of the determinations most required by the sanitary, the tinctorial, and the zymotechnical chemist, find no mention.

The instructions given for the various processes are of a sound, practical character, and, if carefully and conscientiously followed out, will lead to useful results. Hence, in iron- and steel-works, Mr. Arnold's treatise merits full confidence.

Catalogue of Standard Second-hand and New Books, English and Foreign, on Chemistry and the Allied Sciences, Technology, Physical and Electrical Science, Metallurgy, &c. No. 61. 1884-5. William F. Clay, Chemical, Technical, and Scientific Bookseller, University Book Warehouse, 18, Teviot Place, Edinburgh.

We are afresh led to admire the perseverance and business skill with which Mr. Clay continues to obtain rare and valuable works, on terms which enable him to offer them at remarkably liberal prices. We find on this Catalogue complete sets of, *e.g.*, the Chemical News from the very beginning; of the Cavendish Society's publications, which, though now very scarce, are offered at less than one-half the original price; of Liebig's *Annalen*, of *Dingler's Journal*, of Fresenius's *Journal fur Analyt. Chemie*, the *Reports of the British Association* from 1831 to 1888, the *Philosophical Magazine* from the beginning, the *Proceedings of the Royal Society*, &c. These announcements ought to stimulate the Librarians of Universities, learned Societies, &c., into prompt action.

Rare single works are also not wanting, such as the works of Boyle, the papers of J. Clerk Maxwell, the monographs of the late Thomas Carnelley, of C. Schorlemmer. Curious features are the libraries of the late Prince Lucien Buonaparte, and of that of C. O'Neill.

If, by way of contrast, any one wishes to form a collection of the hand-books, manuals, and manualettes of chemistry, in which the English press has been so marvellously fruitful, the Catalogue before us will supply him with the titles.

We think that Mr. Clay's efforts ought to be thoroughly appreciated by chemists and technologists.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 7, February 18, 1895.

Plurality of the Chlorophylls. Remarks on M. Etard's Memoir.—Arm. Gautier.—In 1877 the author established not merely the plurality of the chlorophylls, but their power of crystallising, the total absence of iron and the presence of organic phosphorus and magnesium in the crystals of this substance, which are soluble in carbon disulphide and in ether (see *Comptes Rendus*, cxx., p. 328, and cxix., p. 289).

Agricultural Value of Aluminium Phosphates. Comments on the Memoir of M. Andouard.—Arm. Gautier.—If minervite $(PO_4)_2Al_2,7H_3O$, of bacterial origin, and in general the aluminium phosphates, more or less amorphous, which have had their origin in the decomposition of guanos and other organic matters, and which have derived their alumina from the surrounding rocks, are easily assimilable in the soil, this property cannot be ascribed to the crystalline double calcium and aluminium phosphates of ancient hydro-mineral origin, or to crystalline aluminium phosphates such as gibbsite, wavellite, &c. The phosphoric acid of these minerals, when finely ground, is not more rapidly or more usefully utilised by plants than that of crystalline apatite. My observations and those of M. Andouard apply only to the phosphates which have indirectly originated from the fermentation of nitrogenous matter.

The Determination of Tannic Compounds.—Aimé Girard.—This paper will be inserted *in extenso*.

Remarks on Atomic Weights.—Lecoq de Boisbaudran.—(See p. 116).

Properties of Amorphous Silicon.—M. Vigouroux.—This paper will be inserted in full.

Oxidation of the Tannin of the Cider Apple.—L. Lindet.—We may accept it as an established fact that the oxidation of the tannin of the apple is due to the action of a diastase enclosed in the tissue of the fruit and belonging to the type of the laccases. Further research is required to show whether this is directly due to oxidation, or if it splits up the tannin into molecules more easily oxidised.

Composition and Analysis of Brandies.— . Rocques.—In the analysis of brandies the most definite elements to be recognised are the total amount of volatile substances other than ethylic alcohol, the quantities of ethers and higher alcohols, and the relative proportions of these substance.

Seeds of Moâbi.—H. Lecomte and A. Hébert.—The tree yielding belongs to the family of the *Sagotaceæ*, growing in French Congo. The sap of the bark yields on coagulation a product rich in gutta-percha. The nuts yield from 30 to 35 per cent of a fatty matter. The cake, after the only matter has been dissolved out by benzene, contains 4·05 per cent of nitrogen, and may be valuable as a manure or as cattle food.

Revue Universelle des Mines et de la Metallurgie.
Vol. xxix., No. 1.

New Researches on Chromium.—H. Moissan.—Already inserted.

Atomic Weights of Nickel and Cobalt.—Prof. Winkler (*Zeitsch. fur Anorganische Chemie*).—Already noticed.

MISCELLANEOUS.

Hackney Vestry.—Appointment of Public Analyst.—In an advertisement which appeared in our issue of Feb. 8th the date for receiving applications for this appointment was given as the 18th inst., and for making the appointment the 28th inst. The latter date should have been altered in the next issue to the 27th; but we regret that, instead of this, the date for receiving applications was, by an unfortunate error, altered to the 27th inst.

Certain Derivatives of Phenolphthalein.—A. Hallre and A. Guyot.—Both the procedures employed for the preparation of diethylphthalein yielded one and the same derivative, which does not seem to possess the quinonic grouping. On varying the conditions of the experiment in all possible manners, they never obtained oxime with this ether, nor with the diphenylphthalide of the residue.—*Comptes Rendus*, cxx., No. 6.

Method of Formation of Cyanamide.—Ch. Moureu.—Urea and cyanamide differ from each other by the elements of water. This reaction is fundamentally that which connects the amides to the ammoniacal salts, only in the present case, the amide being cyanamide, the ammoniacal salt, corresponding to ammonium cyanate, is replaced by carbamide or urea. In the same manner as cyanamide has been hydrated and transformed into urea, urea can lose 1 mol. of water and be converted into cyanamide.—*Bull. Soc. Chim. de Paris*, No. 22, 1894.

Researches on Mercuric Picrate.—Raoul Varet.—If the author's thermic values are compared with those obtained by Berthelot for mercury acetate, chloride, and cyanide, other soluble salts of the same metal, we find that the picrate ranks with the acetate, the neutralisation heat of which by HgO liberates +6·0 cal. It will be remarked also that picric acid, in contradistinction to hydrocyanic acid, with potassa displaces it in the solution itself, and without precipitation, liberating +16·7 cal., which answers to a thermic preponderance of the former acid towards this base. On the contrary, with mercury oxide hydrocyanic acid liberates 12·2 cal. for each mol. of acid, which answers to the thermic inversion of the two acids in presence of mercury oxide.—*Bull. Soc. Chim. de Paris*, No. 22, 1894.

MEETINGS FOR THE WEEK.

Monday, 11th.—Medical, 8.30.
Tuesday, 12th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
— Institute of Civil Engineers, 8.
Wednesday, 13th.—Society of Arts, 8. "The Meat Supply of the United Kingdom," by E. Montague Nelson.
— Pharmaceutical, 8.30.
Thursday, 14th.—Royal, 4 30.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
— Society of Arts, 4.30. "Art Tuition," by Prof. Hubert Herkomer, R.A.
Friday, 15th.—Royal Institution, 9. "The Rarer Metals and their Alloys," by Prof. Roberts-Austen, C.B., F.R.S.
— Quekett Club, 8.
Saturday, 16th.—Royal Institution, 3. "Waves and Vibrations," by Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1842.

ISOMERIC NAPHTHALENE DERIVATIVES.*

The Conversion of Sulphochlorides into the Corresponding Chloro-derivatives.

In the case of naphthalene derivatives no interaction is of greater practical importance than that which occurs when sulphochlorides are heated with phosphorus pentachloride, whereby they are converted into chloro-derivatives.

At one time it was argued that reliance could not be placed on this interaction as a means of determining constitution; but of late years no such objection has been raised. and the idea that isomeric change may attend the displacement of the sulphonic radicle by chlorine appears to have been abandoned. The results obtained, especially by Cleve and Dr. Wynne and the writer, are so uniformly consistent, *inter se*, that, bearing in mind the extent of the field covered, there is no longer room for doubt. Observations made during the past year are of interest as throwing light on the nature of the interaction.

There have long been instances on record of the conversion of sulphochlorides into corresponding chloro-derivatives and sulphur dioxide ($RSO_2Cl = RCl + SO_2$) by mere distillation.

The successful use recently made of this method in the writer's laboratory, in preparing chloro- and bromo-derivatives of camphor, by Dr. Kipping and Mr. Pope, has led him and Dr. Wynne to systematically study the behaviour of naphthalene sulphochlorides, which they had long known underwent decomposition, evolving sulphur dioxide, when heated. The conclusion arrived at is that, in all probability, phosphorus pentachloride acts merely by facilitating the resolution of the sulphochloride into sulphur dioxide and the chloro-derivative by attacking the former and converting it into thionyl chloride; and that, in fact, the chlorine in the chloro-derivative is not improbably the original chlorine of the sulphochloride and not chlorine derived from the pentachloride. In most cases the amount of chloro-derivative produced by directly distilling the sulphochloride is inferior to that obtained by means of pentachloride, as the decomposition is facilitated by the chloride, and therefore takes place at a lower temperature in its presence. There is always more or less of a resinoid condensation product formed on distilling the sulphochloride, but the amount is in some cases very small, while in others practically nothing else is obtained. On the other hand, in the case of compounds which are very readily chlorinated, the method permits of the production of chloro-derivatives corresponding to the sulphochlorides, which are almost unprocurable from them by the ordinary method. For example 1 : 1'-chloronaphthalenesulphonic chloride yields a very large proportion of 1 : 1' dichloronaphthalene when distilled, although when heated with phosphorus pentachloride it is almost entirely converted into 1 : 4 : 1' trichloronaphthalene. The α-sulphochlorides appear all to decompose more readily, and to yield a larger proportion of chloro-derivatives than do the β-sulphochlorides. It may be added that, taking into account the readiness with which change occurs during sulphonation, the non-occurrence of isomeric change on distilling sulphochlorides is probably significant.

Bromo-derivatives of Naphthalene.

The conversion of naphthalene sulphobromides into corresponding bromonaphthalenes by means of phosphorus pentabromide is attended with great difficulty, as the bromide frequently acts almost exclusively as a brominating agent, owing to the readiness with which it is resolved into the terbromide and bromine. Far better results are obtained in many cases by merely distilling the sulphobromide, although the formation of higher bromo-derivatives is not entirely avoided. During the year Mr. Jenks and the writer have made considerable progress in completing the series of bromonaphthalenes (di- and tri-derivatives), and in determining the nature of the sulphonic acids prepared from the dibromonaphthalenes by Mr. Rossiter and the writer.

One result of which mention may be made relates to the tribromonaphthalene obtained by Jolin by distilling nitro-1 : 4-dibromonaphthalene with phosphorus pentabromide, which has always been represented as the 1 : 4 : 1-derivative, apparently because it is supposed that, as a rule, α nitro-compounds are formed on nitrating naphthalene derivatives. Judging from the low melting-point of the tribromonaphthalene in question, it is improbable that it is a tri-α-derivative, as such a tribromonaphthalene should melt at a much higher temperature. The accuracy of this conclusion is established by the observation that 1 : 4-dibromonaphthalene hetero-β-sulphonic bromide is converted by distillation into a tribromonaphthalene which is undoubtedly identical with that prepared from nitro-1 : 4-dibromonaphthalene.

Attempts to devise a satisfactory method of preparing 1 : 1'-dibromo-naphrhalene had been made by Mr. Jenks and the writer prior to Meldola's discovery of this modification, and, as these have been continued to a successful issue, reference may be made to the subject. The first method devised involved brominating the acetyl-derivative of Guareschi's 1 : 4'-bromonaphthylamine, prepared by brominating nitronaphthalene, &c.; this readily affords what appears to be a 1 : 1'-dibromacetnaphthalide, but the greatest difficulty has been experienced in hydrolysing this compound.

A second method consists in nitrating 1 : 4-bromonaphthalene sulphochloride. A 1 : 1'-nitrobromosulphochloride is readily obtained, but, although the chief product, it is by no means the only one.

A third and far simpier method consists in heating 1 : 4-bromonaphthalene sulphochloride with bromine, and subsequently hydrolysing the 1 : 1 dibromosulphochloride, which is almost the exclusive product when the operation is properly carried out.

Although it is known that naphthalene hetero-β-sulphonic acid is very readily converted into 1 : 4-dibromonaphthalene hetero-β-sulphonic acid, the order in which the bromine atoms enter has not been determined; and it is, in fact, difficult to arrest the action at an intermediate stage, the tendency to form the dibromo-derivative being very great. Mr. Stallard, however, having kindly placed a quantity of monobrominated β-sulphonate at the writer's disposal, it has been ascertained that it is an α_1-bromo-β_3'-derivative. By heating naphthalene-β-sulphochloride with a molecular proportion of bromine, a very satisfactory amount of 1 : 3'-bromosulphochloride is readily obtained. The "repellent" influence of an acid radicle is clearly brought out by these results, as β-bromonaphthalene yields 1 : 2'-dibromonaphthalene when brominated.

It is well known that there is often great difficulty, especially in the case of α naphthol and α-naphthylamine, in obtaining satisfactory yields of bromo-derivatives, a considerable amount of by-product being formed, the nature of which has not been understood hitherto. Some light has been thrown on the nature of these products by observations made by Mr. Jenks and the writer.

Following the directions given by Cosiner and by Claus and Phillipson, monobrom-β-acetnaphthalide was prepared by mixing bromine with β-acetnaphthalide dis-

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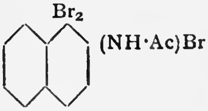
* Eighth Report of the Committee, consisting of Professor W. A. Tilden and Professor H. E. Armstrong (drawn up by Professor Armstrong). Extract from "The British Association for the Advancement of Science," page 268.

solved in acetic acid. Although the conditions were greatly varied, the amounts of pure product obtained were in all cases very unsatisfactory, rarely exceeding 25 per cent. The main product was a crystalline substance, more soluble in alcohol than monobromo-β-acetnaphthalide, but almost insoluble in acetic acid, ethylic acetate, chloroform, xylene, and water. When digested with a weak solution of caustic soda, this substance is converted into monobromo-β-acetnaphthalide, and the same effect is produced by digesting it with a solution of either sulphurous acid or potassium iodide. It appears to be probable that this substance contains the elements of a molecule of bromo-β-acetnaphthalide and a molecule of bromine; such a compound would contain 56·6 per cent of bromine. The highest amount found was 52 per cent, but as the substance undergoes decomposition when recrystallised from alcohol, it cannot be obtained pure. It is not produced by brominating bromo-β-acetnaphthalide, and therefore is probably formed together with it, being perhaps an addition compound, such as is represented by the formula—



By digesting the crude product of the action of a single molecular proportion of bromine on one of β-acetnaphthalide with a weak solution of caustic soda, and then recrystallising from spirit, as much as 75 per cent of the theoretical yield of bromo-β-acetnaphthalide can be obtained.

Rule Expressive of the Formation of Sulphonic Acids.

Dressel and Kothe, in a recent most interesting paper (*Berichte*, 1894, 27, 1193—1210), have taken exception to the "rule" suggested by Dr. Wynne and the writer, referred to in previous reports, that there is an "invincible objection" on the part of two sulphonic groups to *remain* in either contiguous or para- or peri-positions; they have described a tri- and a tetra-sulphonic acid, each containing two sulphonic radicles in contiguous ββ-positions. We shall have occasion to discuss their results when the investigation of the changes attending sulphonation—the most difficult and complex chapter of the subject—is somewhat further advanced. It is only necessary to say that the "rule" was merely an expression of the results up to that time obtained, and was never intended as a final statement.

ON A NEW ELEMENT EXTRACTED FROM RED FRENCH BAUXITE.

(Preliminary Note).

By Dr. R. S. BAYER.

The products of concentration derived from any mineral industry are always an interesting subject of research. We may find in them the presence of substances very different from those which form the principal object of the treatment, and sometimes we may detect novel elements which are still wanting in the periodic series of Mendeleeff.

Such are the dusts of blast-furnaces, the mother-liquors, the substances which remain in the cycle of a manufacture, and we owe the knowledge of a certain number of elements to these processes of concentration. We may mention as instances the discoveries of iodine, bromine, cæsium, rubidium, selenium, thallium, vanadium, &c.

Eight years ago I had occasion to occupy myself with a considerable quantity of a concentration product obtained from the treatment of the red bauxite of the Var. I propose to give here the results, still incomplete, of my researches which my industrial occupation have not given me leisure to complete. I will first say a few words on the origin of the product. In the old procedure for the preparation of pure alumina, the bauxite, finely powdered, was calcined with sodium carbonate or caustic soda in a reverberatory until the formation of sodium aluminate. The mass was dissolved in water, and in the filtered solution of aluminate the aluminium hydroxide was precipitated with carbonic acid. The solution containing the sodium carbonate regenerated was evaporated and served for the treatment of a further quantity of bauxite.

In the calcination of the bauxite there is formed, besides, sodium sulphate on account of the sulphur contained in the coal. After a certain time the quantity of sulphate was such that the mass taken from the furnace was very hard and difficult to dissolve. On this account it became necessary to withdraw from the circulation these lyes of alumina in order to purify them after the precipitation of the alumina with carbonic acid.

This purification was effected by means of successive crystallisations; the mother-liquors were concentrated until they no longer deposited crystals. The last mother-liquors had a specific gravity of 42° B. They were in quantity about 1000 litres, an oily liquid of a deep yellowish brown, and contained all the acids of the metals forming with sodium salts soluble in water. They contained also a small quantity of organic substances.

These lyes were the crude material from which I set out in my researches.

If we further add to these lyes a little caustic soda, we obtain fine yellowish octahedra, which I recognised as the well-known compound of sodium orthovanadate with sodium fluoride, answering to the formula—

$$2Na_3VO_4 \cdot NaFl + 19H_2O.$$

The traces of fluorine contained in the bauxite, and which cannot be manifested by any other process, had accumulated in the soda and given rise to this compound.

More simply, and without any loss of the rare matters, we obtain the same liquids by following my new patent process for the treatment of bauxite. In this process the pulverised bauxite is treated with alkaline liquors, either caustic soda or sodium aluminate decomposed and concentrated up to 45° B.

The alumina alone dissolves, and the ferric oxide, with all other accessory elements, remains in the red residue. If we ignite this residue with about 3 per cent of caustic lime for two to three hours in the oxidising flame of a reverberator, we may extract with water all the sodium salts formed, and thus obtain a yellow solution containing all the above-mentioned elements. There always remains alumina in the state of sodium aluminate; it is preferably precipitated by carbonic acid, and after filtration and washing, the solution is evaporated to crystallise all its salts, until we obtain a liquid of the specific gravity 40° to 42° B.

The qualitative analysis of these mother-liquors showed as the main constituent sodium sulphate and carbonate with notable quantities of chromic and vanadic acids; then molybdic acid and traces of silica, alumina, arsenic acid, phosphoric and tungstic acids, magnesia, lime, &c.

I first precipitated from these solutions the vanadium. For this purpose I added to the liquid a fourth of its volume of water, and after heating to 40° to 50° I added ammonium chloride to saturation. I added further a small excess of ammonium chloride and digested for twenty-four hours, stirring from time to time. At the expiry of this time the chief part of the vanadium was deposited as ammonium vanadate.

On evaporating the liquid and adding a little ammonia, nearly all the rest of the vanadium was precipitated. But as other salts crystallised at the same time, it was necessary to treat the precipitates several times with a little cold water, which dissolves the salts and leaves the ammonium vanadate undissolved.

Still there remains a small quantity of this substance which cannot be removed thus, and of which hereafter.

The liquors thus freed as far as possible from vanadium are boiled with the addition of a little caustic soda, and a current of hydrogen sulphide is introduced until a small specimen filtered gives no precipitate when heated with a little ammonium sulphide. We thus precipitate all the chromium as hydroxide, but the precipitate carries down small quantities of vanadium, phosphoric and arsenic acids, &c. With the greatest precautions it is impossible to precipitate in this manner absolutely pure chrome, when there are other elements in the solution. An exact analysis of researches on this precipitate has yet to be made.

The chromium hydroxide precipitated filters very well; it has not the gelatinous aspect which this substance affects.

We have next to treat the filtrates from the chromium hydroxide. If we proceed as mentioned above the metallic acids are transformed into sulphides only to a small extent. To effect this transformation it is necessary to pass into the solution a current of hydrogen sulphide to complete saturation. If needful we filter again and add to the filtrate hydrochloric acid until the reaction is strongly acid. We stir strongly, and heat when the precipitate agglomerates and can be easily washed by decantation.

The remaining liquids contain nothing remarkable, and may be rejected.

The precipitate, which is dark brown, has especially attracted my attention. In it we have to search for only those elements which form sulphides soluble in the alkaline sulphides. The well-known elements of this class are antimony, arsenic, molybdenum, selenium, tellurium, vanadium, tungsten, and tin. The precious metals belong also to this group, but if there were any they would be left with the iron in the insoluble residues from the attack of the bauxite. Researches carried out have not given any indication of the presence of these metals.

Researches on the Precipitate of the Sulphides.—After desiccation this precipitate appears of an earthy brown; it burns if heated in the air, giving off sulphurous acid and leaving a light brown powder.

If treated with strong nitric acid it is heated to ignition. If thus treated until entirely oxidised it leaves a small quantity of a lemon-yellow precipitate in a deep brown solution. This yellow precipitate is found in great part to be a compound of molybdic and arsenic acids. It is easily soluble in ammonia, and gives with magnesium salts in presence of ammonium salts a greyish white crystalline deposit, and in the liquid we can easily detect molybdenum by its known reactions. But at the same time we may recognise reactions and colourations which lead us to suppose that other researches are necessary.

The brown acid solution still contains vanadium, molybdenum, and also traces of selenium.

The last-mentioned substance is derived without doubt from the pyritic coal used in the calcination, and which contains traces of selenium. It was not possible to show the presence of antimony, tellurium, and tin, but traces of tungsten were found in the yellow precipitate formed by nitric acid.

The crude sulphides precipitated by hydrochloric acid containing always organic matters and sulphur I first ignited after having satisfied myself that none of the other substances were volatilised and that no loss was occasioned. On complete ignition the sulphur, arsenic, and selenium were volatilised almost entirely. The residue of this ignition was then treated with ammonia until nothing further was dissolved, and the slight residue was thrown away as containing nothing remarkable. The filtered ammoniacal liquids were concentrated with the addition of a little ammonia.

Being convinced that ammonium nitrate precipitates ammonium vanadiate well, I added it until the liquid is saturated. We thus separate all the vanadium in the state of ammonium vanadate, which is then removed by filtration.

The filtrate on further concentration deposits several kinds of crystals of an olive-brown and of ammonium molybdate. They may be easily separated, because the former are much less soluble in water than in the latter.

These small crystals contain the new element which I have detected, but they still contain molybdenum. This latter substance may be separated by treating the solution of these crystals in water acidulated with hydrochloric acid with hydrogen sulphide at a temperature of near 70°; the new element is not precipitated by hydrogen snlphide in acid liquids.

The filtrate is then evaporated in the air; at the commencement it is of a violet-blue, but it becomes of a lemon-yellow from the absorption of oxygen.

The small quantity of molybdenum not precipitated is converted into acid. In this state it is precipitated by hydrogen sulphide, and the precipitations and re-oxidations must be repeated until the last precipitate is of a pure white, *i.e.*, free from sulphur.

By this treatment we finally obtain a brown precipitate of molybdenum sulphide and a violet liquid like red wine diluted with water. I satisfied myself repeatedly that the molybdenum sulphide does not carry down any trace of the new element.

The violet liquid, exempt at last from vanadium and molybdenum, contains the new element in the lowest stage of oxidation, whilst the yellow liquid obtained by evaporation in air contains it in the highest state of oxidation.

In this state the substance plays the part of an acid, corresponding probably to the formula R_2O_3, and gives characteristic compounds with the various bases.

The acid itself is soluble in water; on evaporation it deposits a yellow crystalline precipitate, which at a temperature of bright redness melts with difficulty to a brownish yellow mass.

Ammonia converts the acid into a crystalline powder of an olive colour, which dissolves readily in hot water and crystallises in small cubes from the cooling solution. The solution has an olive-green colour, and is precipitated by concentrated ammonia.

I recall here the communication which I made to the Chemical Society of Paris at its meeting of May 28, 1894, in which I gave briefly the results obtained and the reactions of my novel element up to this day.

Hydrogen Sulphide.—I have already spoken of the behaviour of this reagent with acid liquids. I add further that the liquids reduced by hydrogen sulphide, concentrated in a current of hydrogen in the absence of any oxidising agent, give with ammonia a bulky precipitate; this precipitate is of a deep violet-brown, and soon becomes crystalline. The supernatant liquid has always a light violet colour, because the precipitation is not complete.

The solutions of caustic soda and sodium carbonate precipitate these liquids also incompletely; but the precipitates re-dissolve in an excess of the precipitant.

Barium and calcium chlorides, &c., give in concentrated solutions violet-grey precipitates.

Ammonium Sulphide and the other alkaline sulphides give with the yellow liquid solutions of an intense cherry-red. There is formed a sulphur salt from which acids precipitate a sulphide of a rust colour. But with the utmost precautions we cannot render the precipitation complete; the supernatant liquid remains of a rust colour.

Barium Chloride gives in the ammoniacal solutions of the salts a greenish yellow precipitate easily soluble in acids and forming a light yellow liquid.

Mercurous Nitrate gives a straw-coloured precipitate soluble in nitric acid; warty crystals are obtained from the solution.

Silver Nitrate gives a green precipitate. This precipitate is soluble in nitric acid and also in ammonia. If the solution in the latter reagent is effected in heat, the silver salt crystallises out on cooling.

Magnesium Chloride in an ammoniacal solution with the addition of ammonium chloride gives at first no precipitate; after some time, and especially if the sides of the glass are rubbed, there is formed a characteristic green precipitate analogous to that of phosphoric acid. Slow precipitation yields crystals large enough to be recognised with the lens. The separation is almost complete, and the liquid, which is green at first, becomes quite decolourised. Yet barium chloride still produces a slight greyish precipitate.

Molybdic Liquor gives in solutions acidified with nitric acid a yellowish white precipitate which deposits with difficulty. The precipitation is very incomplete, and the liquid remains of a strong yellow colour.

Hydrogen Peroxide gives no change of colour either in the acid or the alkaline solutions. It is well known that this reagent gives a very decided reaction with vanadium.

Potassium Ferrocyanide.—This reagent, very sensitive for vanadium and molybdenum, occasions no change in the solutions.

The chlorides of the new element seem to be volatile. From a solution which contained much ammonium chloride to separate the vanadium, I attempted to expel the ammonium salts by volatilisation. In this operation I observed notable losses of the rare element in the state of chloride. There was formed a yellow sublimate, soluble in water, and the vapours escaping from the crucible formed, with the watery vapour from the flame gases, a faint violet-brown light between the crucible and its cover.

I regret to say that it has not yet been practicable to collect enough of the substance for quantitative determinations. From 1 million kilos. of bauxite I have been able to obtain only about 2 grms. of the ammonium salt. Nevertheless I believe that there are serious reasons to infer the discovery of a new element. The spectroscopic examination has shown very characteristic rays in the green, the blue, and the violet.

From want of time and of sufficient apparatus these rays have not yet been determined with sufficient precision. I hope that after some time I shall be able to prepare matter sufficient for a determination of the atomic weight, to affect analysis of the characteristic salts and the determinations which are still wanting.

On the Red Ferruginous Residue from the Treatment of Bauxite.—After having extracted all the acids by calcination with lime, and thoroughly washed the residue, the latter is not yet pure ferric oxide. It still contains numerous elements in addition to iron and aluminium. I have ascertained the presence of silicon, calcium, magnesium, manganese, phosphorus, and titanium. The last-named element is present in combination with sodium, and as $NaHTiO_3$, and may be extracted almost entirely with a little silica, which is found in a double combination with soda and alumina—

$$(Al_2Na_2.Si_3O_{10}+9H_2O).$$

It is sufficient to treat it with weak sulphuric acid containing 8 to 10 per cent of H_2SO_4. We digest for three or four hours at a temperature not exceeding 50°, stirring from time to time.

The filtrate is then boiled with the addition of a little sodium bisulphite, and, after dilution, with an equal volume of water. It is advisable to boil it for 1½ to 2 hours in a wooden trough lined with lead, by direct steam. The titanic acid is deposited almost pure, and it may be purified by known methods.

There are still doubtless other elements in this residue, but the difficulty has been to separate them from the iron and to treat considerable masses of these residues.—*Bull. de la Soc. Chim. de Paris*, Series 3, xi. and xii., No. 24.

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.*

By AMOS PEASLEE BROWN.

(Continued from p. 121).

A. A. Julien (*Ann. N. Y. Acad. Sci.*, iv., pp. 154, 155) has shown that different samples of pyrite show a difference in their reaction with bromine vapour. His experiments consisted in exposing finely ground pyrite to the action of bromine vapour at the temperature of the air for twelve hours. The residue was extracted with dilute H_2SO_4, which removed the iron rendered soluble (bromide), and the iron was then determined in this solution. The percentage of iron that had dissolved varied from 2·43 to 15·20 per cent, although all samples tested are described as pyrite. He also tried the action of bromine in aqueous solution, but the reaction was too rapid to give any comparative results.

Much more important are the results obtained in the oxidation of these minerals by the electric current as conducted by Prof. Edgar F. Smith (*Journ. Franklin Inst.*, cxxx., pp. 152—154), and it was the remarkable results that were then obtained that induced me to continue the study of the comparative reactions of these two minerals. Smith found that a current which would completely oxidise the sulphur in marcasite in a given time would oxidise less than half of the sulphur in pyrite in the same time. This remaining sulphur was held very tenaciously, though the mineral was subjected to more powerful currents and longer continued action than in the case of marcasite or pyrrhotite. Finally, by adding an equal quantity of CuO, and using a more powerful current, all of the contained sulphur was oxidised. Previous to the addition of CuO but 21 or 22 per cent of the sulphur was oxidised. In concluding the article above referred to, the author questions whether the crystalline form alone can make this difference in the action of the two minerals when under the influence of the current.

The two samples of pyrite and marcasite that I selected for the following study were chosen after considerable examination of material as being typical of the two forms of FeS_2. The pyrite was from the hematite mines of Elba. It is exceptionally pure, and free from decomposition or tarnish. Before deciding on it finally pieces were ground and polished, and then examined under the microscope with powers ranging from 50 to 200 diameters, in order to see if it contained any enclosures or varied in texture. It was perfectly homogeneous and showed no enclosures. It took a high polish. The crystals showed the combination of octahedron and pentagonal dodecahedron $O+\frac{{}^{2}O^{\infty}}{2}$. Some of the crystals were coated in places with scales of hematite, but this was all carefully removed in breaking up material for experiment. The colour was bright brass-yellow; the specific gravity was determined as 5·179. The marcasite was from the zinc mines of the Subcarboniferous of Joplin, Jasper County, Mo., finely crystallised in polysynthetic twinnings. The freshly-broken crystals show a greenish yellow colour, almost white, but they tarnish readily with bluish or brownish colours. No gangue was present, everything dissolving completely in nitric acid. This marcasite was examined with the microscope in the same way as the pyrite; it did not take such a high polish on account of a fibrous structure, but no foreign matter was found with a power of 200 diameters. Its colour was uniform throughout, showing that no pyrite was present. The specific gravity as determined was 4·844.

In preparing material for experiment only sufficient was ground for immediate use to avoid any chance of oxidation of the ground material; the stock samples of the two minerals broken to nut size were kept in stoppered

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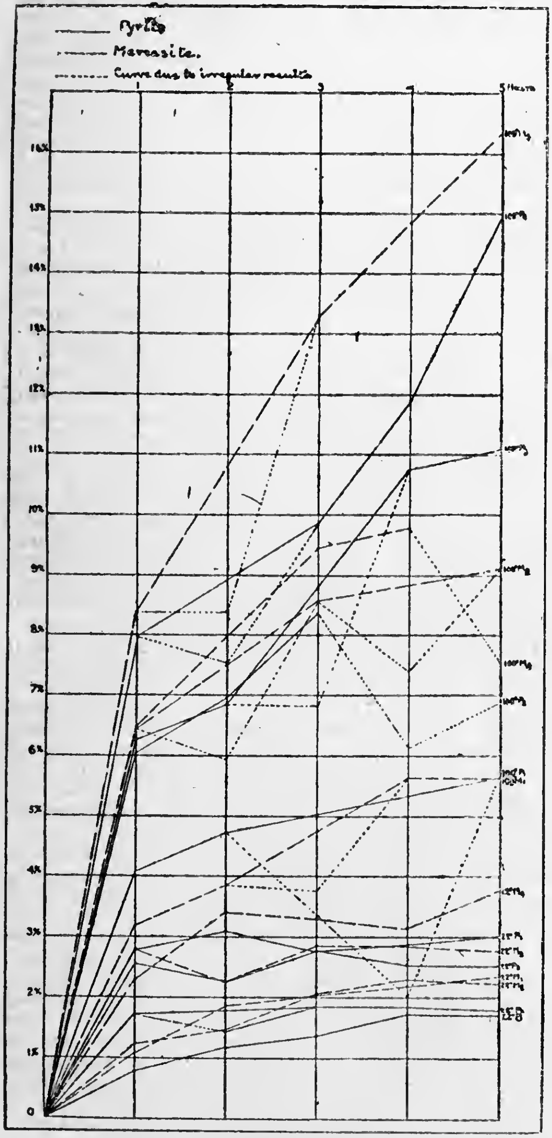
* Read before the American Philosophical Society, May 18, 1894.—From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

bottles. The grinding of material was continued as long as grit appeared, but no bolting was resorted to.

As the experiments of Prof. Smith on oxidation by the electric current showed such remarkable results, my first experiments were on oxidation. As an oxidising agent potassium permanganate ($KMnO_4$) was used, several strengths of which were tried for varying intervals of time with each mineral, and the amount of sulphur oxidised to sulphuric acid determined in the liquid by precipitating as barium sulphate. The object was to secure a complete series of results which would show the comparative rates of oxidation of the sulphur in the two minerals. Neutral aqueous solutions of the potassium permanganate were used, and the strengths of solution employed were $\frac{1}{100}$ normal, 1 per cent, 3 per cent, and 5 per cent; the periods of oxidation extending over one, two, three, four, and five hours, and the entire series being performed at ordinary temperatures and at 100°. As duplicate determinations were made in the majority of cases (I made about 130 determinations of sulphur as barium sulphate), this work consumed a large amount of time, and prevented as full a study of some other reactions of the two minerals as had been originally intended. The following are the detailed descriptions of my processes and results:—

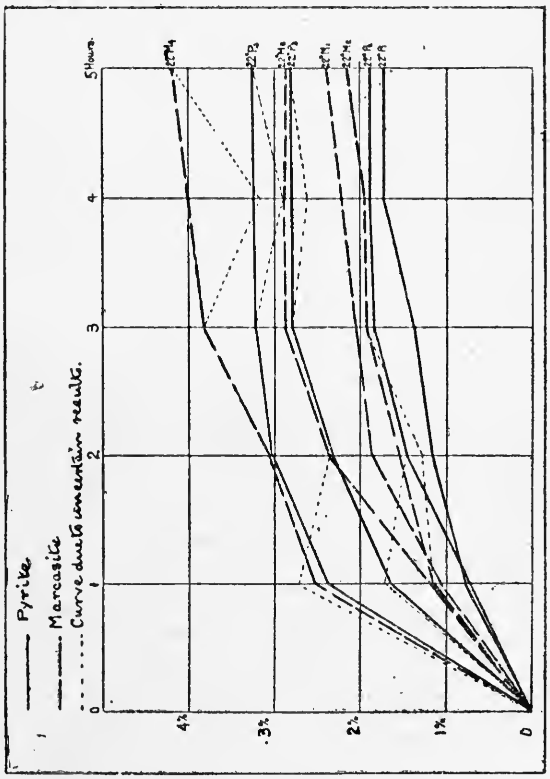
Proceedings Amer. Philos. Soc. Vol. XXXIII, No. 145. Plate XVII.



Action of $\frac{1}{100}$ Normal Potassium Permanganate Solution at Ordinary Temperature.

These oxidations were performed as follows:—Two-tenths of a grm. of the finely powdered mineral was placed in a stoppered bottle of about 100 c.c. capacity, then 50 c.c. of the permanganate solution added, and the contents of the bottle violently shaken to break up lumps. This shaking was repeated about every fifteen minutes while the oxidation lasted. The temperature of the room was at the same time recorded. As stated, the oxidation was continued for one, two, three, four, and five hours with each mineral, making at least ten experiments necessary for each strength of solution. After the solution had acted for the required time it was rapidly filtered through asbestos with aid of the filter pump, the filtrate transferred to a beaker, 20 c.c. of concentrated hydrochloric acid added, and the whole heated until all manganese was reduced to manganous chloride. If not too acid the solution was then diluted to about 300 c.c., and the sulphuric acid precipitated as barium sulphate. When very acid excess of hydrochloric acid was removed by evaporation or by adding ammonia, the ammonium chloride seeming to facilitate the precipitation. The precipitate was washed with hot water and then weighed. All precipitations were made at boiling temperature and digested hot for at least two hours, and then cold for at least twelve hours more before filtering. The filtrates from most of the cold tests were reduced with metallic zinc and titrated with permanganate, but no iron was found in the solution.

Proceedings Amer. Philos. Soc. Vol. XXXIII. No. 145. Plate XVIII.



The two minerals did not present the same appearance when acted on by the oxidant. Pyrite retained its colour and seemed as pulverulent as when the permanganate was added, but marcasite immediately on the addition of the reagent became coated with manganese dioxide, took on a brownish colour, and showed a tendency to cake together and stick to the sides of the bottle, so that it was with difficulty dislodged. This tendency of the marcasite was more marked with stronger solutions of the permanganate, and was doubtless the cause of much of the irregularity that will be noticed in the results. The reason for this difference in action of the reagent on the two minerals will be discussed later on.

The percentages of sulphur oxidised in the two minerals by this method are shown in the following Table, where all results that were obtained are recorded. The figures show the percentages of sulphur oxidised, calculated on the basis of FeS_2 equal to 100 per cent. It will be noted that the four-hour oxidation of marcasite shows a result that is less than the two-hour. This was due to caking of the mineral against the walls of the bottle, which prevented much of it from coming in contact with the solution. On the whole, this series was about the most satisfactory of the cold experiments with $KMnO_4$, the action of this dilute solution being less rapid, and hence more even than that of the more concentrated solutions; naturally the action ceases with a certain dilution, and hence the four- and five-hour oxidations of pyrite are about equal.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a $\frac{1}{100}$ N. Solution of $KMnO_4$ at 22°.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with $\frac{1}{100}$ N. solution $KMnO_4$ ..	0·78	1·17	1·38	1·74	1·72
Marcasite with $\frac{1}{100}$ N. solution $KMnO_4$ ..	1·07	1·86	2·04	(1·25)	2·38

The curves formed by plotting these results on rectangular co-ordinates are shown in Pls. xvii. and xviii. They are marked 22° M_1 for the marcasite, and 22° P_1 for the pyrite.

Action of 1 per cent Potassium Permanganate Solution at Ordinary Temperature.

This and also the two following series were performed as described under $\frac{1}{100}$ normal solution above. At least two experiments were tried with each mineral in this and the two following cold oxidations, and whenever a result was notably higher or lower than its duplicate a third or fourth was tried. The tendency of the marcasite to cake, noted in the previous series, became still more marked here, and is doubtless the cause of one of the four-hour oxidations (marked by parenthesis) being notably lower than the three-hour. Such a result is obviously incorrect. On the other hand, the result in the three-hour column which is placed in parenthesis is the highest obtained. This experiment was made at the same time as the one showing 1·93 per cent, but the room was very warm (25°), which may in part account for this high result. It will be noticed that the oxidation of the pyrite seems to stop at the three-hour trial, those following showing no appreciable increase. This is well seen in the graphic representation of these oxidations (Pls. xvii. and xviii.).

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 1 per cent Solution of $KMnO_4$ at 22°.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with 1 per cent solution $KMnO_4$ cold	1·72	1·38	1·85	1·79	1·70
	1·71	1·47	1·87	1·90	1·89
Marcasite with 1 per cent solution $KMnO_4$ cold ..	1·16	1·29	1·93	1·95	2·01
	1·28	1·13	2·19	(1·56)	2·15
			(3·92)	2·69	2·55

(To be continued).

ON THE ESTIMATION OF SULPHUR IN PYRITES.*

By G. LUNGE.

UNDER the above title, Mr. T. S. Gladding (*Journ. Am. Chem. Soc.*, June, 1894; CHEM. NEWS, lxx., p. 181) has published several modifications of the wet assay of pyrites which call for some comment on my part, since these modifications purport to be improvements on my method, contained in the "Alkali-Makers' Handbook," and extensively employed in all countries.

Some of Gladding's modifications are of a less important character, and these can be passed in review very briefly. He does not, like myself, test the sample with its natural moisture, estimating the latter in a special sample, but he dries the whole sample and weighs it out in that state. He employs a whole grm. of pyrites, I only half a grm.: and I do so purposely, because the washing of the precipitates is much easier, and consequently the results are more reliable with the smaller than with the larger quantity. In lieu of the mixture of acids employed by me (3 volumes of nitric acid of sp. gr. 1·42, and 1 vol. of fuming hydrochloric acid), Gladding decomposes the pyrites with a solution of bromine and nitric acid. The prescription for that solution is not correct as printed, for 75 grms. of potassium bromide cannot possibly be dissolved in 50 grms. of cold water, or anything like that quantity; but this may be a clerical error, which does not matter very much, as ultimately the solution is diluted to 500 c.c. I will say at once that the bromine solution works well, but no better than the acid mixture according to my prescription.

A more important modification is the following:—It is well known that in the presence of iron the precipitate formed by barium chloride in a solution of sulphates cannot be freed from iron, and that the results of the estimation of sulphur in this case are too low; in my publication of 1879 (*Zeitschr. Anal. Chem.*, xix., 419) I found on the average 0·19 per cent too little sulphur, unless the iron had been previously removed from the solution. Fresenius has also worked on this subject, and Jannasch and Richards, in 1889, completely elucidated it by proving that a double sulphate of barium and iron was formed in this case. Gladding gives a similar explanation, without mentioning the more complete investigations of his predecessors, which would have saved him the trouble of working out the matter for himself. I had already long ago dealt with that difficulty by proposing, in 1889, that method which was afterwards embodied in the "Alkali-Makers' Handbook," viz., precipitating the iron by ammonia, washing the ferric hydroxide, and precipitating the sulphate in the filtrate by barium chloride. Gladding asserts, however, that "the most careful washing failed to wash out all the sulphur from the ferric hydroxide," and he therefore proposes to wash the hydroxide as well as possible and to dissolve it afterwards in diluted hydrochloric acid, thereupon treating that solution with barium chloride; evidently with the tacit assumption that the small quantity of sulphide present in that solution is accurately enough estimated as barium sulphate, in spite of the large quantity of iron present; but that assumption is far from self-evident, nor does it actually represent the truth, as we shall see.

It is quite evident that Gladding, although he knows and quotes the "Alkali-Makers' Handbook," and although he entirely adopts the prescription given there (p. 93) for the *precipitation* of the ferric hydroxide, which deviates not unessentially from those previously given by Fresenius and others, has not completely followed the instructions for the *washing* of the precipitate given immediately after in the following words:—"Filter hot, and wash on the filter with hot water, avoiding channels in the mass, but

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* Read at the Boston Meeting, December 28, 1894.—*Journal of the American Chemical Society*, xvii., No. 3.

so that the whole precipitate is thoroughly *churned up* with the water each time." Many hundreds of pyrites tests made in my own and other laboratories have proved that by following the above instructions the washing of the ferric hydroxide is accomplished in from half an hour to an hour, that the number of washings need not exceed five, and the bulk of the liquid, apart from the original filtrate, need not exceed 100 to 150 c.c., and *that no trace of sulphur is left in the ferric hydroxide*, as evidenced by drying the precipitate, fluxing it with pure soda, dissolving it in water, and testing the solution for sulphate. It is true that the students in my laboratory have sometimes failed to get out all the sulphur, but in *every* case through having washed in the usual way, instead of that described above; and the same men have succeeded in *every* case, after their attention had been drawn to this point.

There is another difference between Gladding's and my own manner of proceeding. I prescribe heating the solution of the sulphate to the boiling-point, as well as that of the barium chloride, adding the latter to the former all at once, allowing to stand for half an hour only, and then at once filtering and washing while the liquid is quite hot. I had convinced myself that under these circumstances the precipitate filters most easily, and no barium sulphate whatever subsequently separates from the filtrate. Gladding, however, not merely adheres to the old and useless prescription of letting the liquid stand over night after the precipitation, but he adds to this a novel and most tedious way of effecting the precipitation, viz., adding 50 c.c. of barium chloride solution quite slowly, one drop per minute. This will take about an hour, instead of a few seconds, as in my method.

I considered it my duty to find out whether the method recommended by Gladding is better than mine, or inferior to it, or equivalent with it; and in the last case, which of the two is easier and quicker to execute. For this purpose a sample of Spanish pyrites was selected which was triturated as usual, and mixed in the most careful manner. The tests were made by one of my demonstrators, H. von Keler, under my constant personal supervision. First of all the sample was tested exactly according to the method laid down in the "Handbook," with the following results: — 50·17; 50·42; 50·20; 50·23; 50·19; average, 50·24 per cent. The insoluble amounted to 1·42 per cent; the moisture to 0·47 per cent. I abstain from reducing the percentages to the dry state, as being unnecessary in this case.

As the next step, a number of samples were decomposed by Gladding's mixture of bromine solution and nitric acid. We found his prescription in this item to be perfectly correct; it is not feasible to hasten the process (which is much lengthier than that used by myself), for instance, by filling the water-bath from the first with hot water. Any attempt to do such a thing ends in an over-violent reaction, and a loss by spurting and separation of free sulphur. We tested, of course, our bromine and potassium bromide, and found them quite free from sulphuric acid.

Three of the samples thus decomposed, according to Gladding, were precipitated exactly according to his method (one hour's precipitation, twelve hours' settling); another three samples according to mine (precipitating all at once and filtering after half an hour). The results were:—

Gladding's Method.	Lunge's Method.
50·24	50·24
50·24	50·22
50·30	50·28
50·26	50·25

We see that both methods of precipitation give identical results, and these also entirely agree with the tests made from the first according to the "Handbook" method, viz., 50·24. The conclusions to be drawn therefrom are:—1. Since both methods of precipitation yield the same result, my expeditious method of precipitation and filtration, which, inclusive of washing, takes about an hour, is preferable to Gladding's method, requiring about twelve hours. 2. Since Gladding's bromine method for decomposing pyrites yields results identical with that prescribed by myself, there is no reason for abandoning the latter and adopting a more tedious method, unnecessarily employing such a disagreeable reagent as bromine.

I understand from a private communication of Mr. Gladding's that he attributes the greatest value to his manner of precipitating the barium sulphate, and that in his opinion by operating in my way barium chloride is always carried down with the sulphate, making the results too high by 0·20 to 0·40 per cent. It would have been most remarkable if that point had been overlooked in the many thousands of tests made according to my methods by perhaps a hundred different chemists; but in order not to incur any reproach, I had this point put to another searching investigation. Mr. W. Jackson made five most careful tests of another sample of pyrites, decomposing and otherwise treating them absolutely in the same way, but making the precipitation in two cases by Gladding's and in three cases by my method. The results were:—

	Lunge's Method.		Gladding's Method.
	50·59 per cent.		50·60 per cent.
	50·63 ,,		50·66 ,,
	50·56 ,,		—
Average,	50·59 ,,	Average,	50·63 ,,

This affords another thorough refutation of Gladding's assertion.

In all analyses made up to this point the ferric hydroxide had been precipitated and washed five times exactly in the way described by me; in every case it had been afterwards tested by fluxing with soda, but no trace of sulphur had ever been found. This furnished an additional (although unnecessary) proof that Gladding's assertion in that respect is equally unfounded, and that the treatment described by him (dissolving the ferric hydroxide in hydrochloric acid and precipitating by barium chloride) is quite useless when observing the precautions in washing pointed out by me. Still I thought it advisable to find out how Gladding's process would work in cases where, by some mistake, a little sulphur had been left in the hydroxide, and I grant that in important cases the latter ought to be tested in some way or another for any sulphur left behind. I further grant at once that in this case Gladding's method, as described, is more expeditious than mine: drying the ferric hydroxide, detaching it from the paper, mixing it with pure sodium carbonate, fluxing it in a platinum crucible (in such manner that no sulphur from the gas can get into the mass, *e g.*, in a hole made in asbestos cardboard), dissolving in water, and precipitating the sulphur by barium chloride. It is hardly necessary to say that I did not choose this plan without first considering the very simple method described by Mr. Gladding; but I rejected it, since Fresenius had proved that barium sulphate is very distinctly soluble in an acid solution of ferric chloride. But as Gladding now asserts that the direct solution of the ferric hydroxide in hydrochloric acid yields accurate results, it became incumbent upon me to examine this statement.

Eight samples of our pyrites were decomposed, and the ferric hydroxide was precipitated under absolutely equal conditions of dilution, temperature, and quantities of reagents. The washing was purposely not continued as far as it ought to have been; and as some previous experiments had shown that no uniform degree of exhaustion can be attained by incomplete washing, we estimated in all cases the *total* sulphur, separating, of course, that which was found in the filtrate and that which was left with the ferric hydroxide. Four of the eight samples were treated by Gladding's prescription, and four by my own system. The results were:—

Lunge (fluxing with sodium carbonate).			Gladding (dissolving in hydrochloric acid).		
Filtrate.	Precipitate.	Total.	Filtrate.	Precipitate.	Total.
49·64	0·60	50·24	48·98	1·03	50·01
49·36	1·01	50·37	48·84	1·39	50·23
49·07	1·21	50·28	49·02	1·07	50·19
49·25	1·04	50·29	49·30	0·73	50·03
Average ..		50·29	Average ..		50·09

This proves that Gladding's method does not, in this particular, give accurate, but *low* results (by 0·20 per cent); with less complete washing the discrepancy would evidently have been even greater. The total sulphur found by my process, on the other hand, agrees quite satisfactorily with the correct analyses quoted before.

The final conclusion of this investigation must be:—That in most points Gladding's method is correct, but in *not a single case* more so than my method; his modifications cannot be approved, as they greatly lengthen the time required for the analysis, without any corresponding advantage whatever. In one point which forms the principal novelty in Gladding's process, he is decidedly *wrong*. It is not true that it is unavoidable to leave any sulphur in the ferric hydroxide; on the contrary, this is very easy to avoid. If it has, after all, happened by incorrect manipulation; Gladding's plan will *not* get out all the sulphur, but my plan (fluxing with soda) must be adopted.

I have shown that there is not a single point recommended by Gladding, in deviation from my method, which is fit for adoption, and I must conscientiously advise my brother chemists to adhere to the method just as I have laid it down in the "Alkali-Makers' Handbook."

In conclusion, I would add that I have also tried the method recommended by F. Johnson (Chem. News, vol. lxx., p. 212), omitting to precipitate the iron, but reducing it by sodium hypophosphite to the state of protochloride. Even when working precisely as described by the author, the results were so widely off the truth, that I can make nothing whatever of this plan.

ON THE CORROSION OF ALUMINIUM.

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

In order to ascertain the effects of the weather upon ordinary sheet aluminium, two shallow dishes were made of 1/25 inch gauge metal, of the best commercial quality, and exposed on the roof of the laboratory from Nov. 23rd, 1893, to Dec. 7th, 1894, or fifty-four weeks.

The metal was made into basins so as to catch rainwater, and to give the salts, &c., which it might have in solution, an opportunity to act upon the metal.

The metal very soon lost its brilliancy, and became somewhat rough and speckled with grey spots mixed with larger light grey patches; it also became rough to the feel, the grey parts could be seen to distinctly project above the surface, and under the microscope they presented a blistered appearance. This incrustation is held tenaciously, and does not wash off, neither is it removed on rubbing with a cloth.

The raised parts are probably due to the formation of a hydrated oxide, but I am leaving the determination of the composition of this until I have a larger quantity at my disposal.

Contrary to my expectations, the cups had not lost weight, but had even increased. One, weighing 13·91 grms, had increased by 0·104 grm.; and the other, weighing 13·865 grms., increased by 0·080 grm. After boiling in water for some hours, and rubbing, the first still showed an increase of 0·077 grm., and the second of 0·055 grm.

To ascertain the effects of common salt, a plate of the same metal, 3×4 inches, and weighing 19·829 grms., was repeatedly dipped in a solution of sodium chloride and allowed to dry for three months; this lost 0·019 grm., and, after washing and rubbing dry, 0·059 grm.

One reason for making these experiments is, that Mr. H. C. Russell, C.M.G., F.R.S., the Government Astronomer, some years ago tried aluminium cups for a raingauge, but found that they were so quickly corroded through that he had to relinquish the use of the metal (if they had been gilt they might, however, have answered well enough); then, too, it is a very common thing to see aluminium recommended for certain architectural work, on account of its lightness and its assumed permanent lustre; this assumption being due to the statements, repeated from book to book, that aluminium is unaltered by exposure to the air, to the action of water, hydrogen sulphide, and only slightly by dilute acids (even in such works as "Aluminium," by Joseph W. Richards, M A.; London, 1890).

The absolutely pure metal may be permanent in the air, but the best aluminium ordinarily obtainable is in that respect very little, if at all, superior to zinc.

The commercial metal, as we have seen, does not retain its lustre, but very rapidly acquires the appearance of old zinc.

Recently it has been found, also, that aluminium is acted upon by sea-water; it is therefore not so perfect a material for torpedo and other boats as was previously thought.

Hence the prevalent idea that aluminium is a metal resembling gold or silver in the property of not oxidising must be relinquished.

NOTICES OF BOOKS.

City and Guilds of London Institute for the Advancement of Technical Education. Head Office: Gresham College, Basinghall Street. Report on the Central Technical College, Exhibition Road, S.W. Session 1893—1894.

We have to notice with satisfaction the recent change of name of this establishment. Instead of "Central Institution" it is now called more intelligibly the "Central Technical College." A decrease in the number of candidates seeking admission has been observed during the two past years. In 1892 it is remarked the number of candidates for admission was 107; in 1893, 102; and in 1894, only 88. It is pointed out as a consolation that the proportion of the rejected applicants has declined, so that the number actually admitted has not fallen off. We are also reminded that since the College was first opened the facilities for obtaining technical education have been strikingly increased. A further cause, which may or may not be permanent, is the overcrowding of the professions for which a technical training is necessary.

Among the various departments Chemistry, as usual, fares the worst. Of the thirty third-year's students recommended for the diploma of Associate of the Institution, three only had taken Chemistry as their subject.

The difficulty of finding employment for past students is very great, and is, we fear, increasing. "A large proproportion of students of the year have only been able to begin their practical career by paying a premium to be received as pupils!" Hence the training received at the College seems to have a minus value in the eyes of employers. This is fearfully disheartening, and goes far to explain the falling off in the number of candidates seeking admission. What is the prospect for youths whose friends are not able to buy them positions in industrial establishments? Perhaps a part of the difficulty springs from the low value which English practical men set upon theoretical knowledge.

A very important feature in this report is that it traces the subsequent career of past students. This is something more worthy to be called "results" than are the lists of pupils advertised by schools as having passed this or that examination. Of these the chemists figure as a small fraction in comparison with the physicists and engineers. If we might suggest, it seems to us that the list of past students might be further improved by the mention of any discoveries or inventions which they have made.

Report on the Result of Investigations on the Micro-Organisms of Sewage. Part I.—Their Relation to those of Sewer Air. Part II.—Observations on the Bacillus of Typhoid Fever and its Relation to Sewage. By J. Parry Laws, F.I.C., and F. W. Andrewes, M.B., M.R.C.P.

These investigations, undertaken by the authority of the London County Council, will prove very valuable contributions to Sanitary Science.

The authors have made a great number of experiments with sewage from the Smithfield outfall from St. Bartholomew's Hospital, from the Fleet sewer, from the Barking outfall, from the Crossness outfall, and from the drain which serves the scarlet or typhoid fever blocks at the Eastern Fever Hospital at Homerton.

The selection of these localities must be pronounced judicious; every care has been taken to obtain fair average specimens of the sewage, and the experiments have been performed *secundum artem.* We may therefore receive the Report with a great degree of confidence.

The conclusions drawn are that sewer air has not the power of taking up micro-organisms from the sewage. The organisms which are most abundant in sewage are precisely those which are absent from sewer air. The authors of course admit that sewage is a common medium for the dissemination of typhoid fever; they consider it possible that polluted soils—*i. e.*, such as have been saturated with sewage—may give up germs to the subsoil air, but the supposition that the air of the sewers plays a part in the conveyance of typhoid fevers seems to them highly unlikely.

A mixture of the four non-pathogenic bacteria did not appear to promote the extinction of *Bacillus typhosus*, but had rather a reverse action. In one flask, which contained the four species *Bacillus fluorescens stercoralis*, *B. fluorescens liquefaciens*, *B. albus putridus*, and *B. cloacæ fluorescens*, some typhoid bacilli were found living even after the lapse of thirty days! This fact certainly does not justify any carelessness in the admission of sewage to drinking waters or articles of food.

We are as yet very far from having eliminated zymotic disease, even from the home-kingdoms.

Researches on the Arseniates, Phosphates, and Modifications of Phosphoric Acid. By Thomas Graham, F.R.S. (1833). Edinburgh: W. F. Clay, Teviot Place. London: Simpkin, Marshall, and Co. (Ltd.) 1895.

This little book forms one of the series of "Alembic Club Reprints," and certainly contains Graham's most important contribution to chemical science. The research here expounded appeared in the *Philosophical Transactions of the Royal Society* for 1833, and certainly, as it is pointed out in the Preface, contained the starting-point of the idea of the Basicity of Acids. It first revealed the mutual relations of the ortho-, pyro-, and metaphosphoric acids, and of their corresponding salts. The author expresses the opinion that there is, indeed, only one phosphoric acid, and that its modifications are due exclusively to the different proportions of water combined with the acid. The recognition of their distinctive characters was very fruitful, and has led the way to important results.

CORRESPONDENCE.

DE BOISBAUDRAN'S SYSTEM.

To the Editor of the Chemical News.

Sir,—From time to time chemists have been edified or tantalised with references to or promises of a "system" which M. Lecoq de Boisbaudran has elaborated, but which seems not yet ripe for publication. May we hope from a paper in the *Comptes Rendus*, which you have reproduced in the last number of the Chemical News, that the distinguished author will at last break silence and give the scientific world an opportunity of judging on the real scope and the capabilities of this long promised system?—I am, &c.,

J. W.S.

"YEAR-BOOK OF PHARMACY."

To the Editor of the Chemical News.

Sir,—In the *Year-Book of Pharmacy*, 1871, p. 628, the Chairman of the Dinner of the Pharmaceutical Conference, in introducing the toast "Success to the British Pharmaceutical Conference," stated "Last year the Conference issued, the *Year-Book of Pharmacy.*—(Cheers). The Chemical Society has already copied our example; and those who were present at the inaugural address of Sir William Thomson last night are aware that a similar undertaking is proposed to be carried out by the British Association." Dr. Alexander Wood mentioned this matter too (p. 630).

Although knowing much of the publications of most of the Chemical and allied Societies, I know nothing of either of these works, and should be glad if some correspondent can give me any information respecting them. The reference cannot be to the Journals of the two Societies, for both had been running many years previous to 1870.—I am, &c.,

J. Cuthbert Welch.

The Laboratory, The Brewery,
Reading, March 3, 1895.

BORON CARBON BATTERY.

To the Editor of the Chemical News.

Sir,—Mr. H. N. Warren (Chem. News, lxxi., p. 87) asks me where I "obtained the information from as regards the existence of a platinum element" in his battery, "while at the same time the title of the battery is distinctly stated 'the boron carbon battery.'" I will say, in reply, that my only source of information was his own description in the Chemical News (vol. lxxi., p. 2). The information was not contained in the "title of the battery," and I did not look for it there. It is contained in the following sentence:—"The cells themselves are constructed on the flat system, with sliding carbon plates enclosed in teak-wood boxes, the carbons being chemically prepared by special treatment, whereby gaseous compounds of boron are so decomposed as to allow of the boron becoming absorbed into the pores of the carbon, which are afterwards soaked in solution of oxalate of platinum, and heated to redness in an atmosphere of hydrogen." If Mr. Warren can make carbon elements by this process that do not contain a considerable quantity of platinum he has wrought a greater "revolution" in chemistry than any he has yet pointed out in voltaic electricity.

My former criticism was not intended to disparage Mr. Warren's efforts, as he seems to suppose. but rather as an expression of regret that he did not, in connection with his claims, give some intelligible data from which it would be possible to compare his battery with others, as he does not describe the battery so that others could prepare it and verify the results. The only datum he gives is that the electromotive force is 3 volts. This in itself is nothing remarkable, nor does it signify any revolution in voltaic electricity. He adds the very ambiguous statement, "and giving a constant current from 2 to 2·5 for an almost unlimited duration." The natural inference is that he means 2 to 2·5 ampères. If he means that he obtains a constant current of 2 ampères for more than about 188 hours by the consumption of one pound of zinc, it means perpetual motion. If he means that he obtains 2 ampères for 188 hours or something less by the consumption of one pound of zinc, then he has not accomplished anything revolutionary.

The question of most importance, it seems to me, is not whether this is a "Yankee bull" or an "English calf," but whether Mr. Warren is going to revolutionise voltaic electricity. I invite him again, therefore, if he has anything further to say on the subject, to give at least some definite data showing what his battery will do.—I am, &c.,

C. J. Reed.

441, Chestnut St., Philadelphia.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 8, February 25, 1895.

Ebullioscopic Study of certain Colouring Derivatives of Triphenylmethane.—A. Haller and P. Th. Muller.—The authors refer to the discussion concerning these compounds. Some chemists, such as O. and E. Fischer, Nietzki, Bernthsen, &c., imbued with the very seducing theory of the chromophoric groups introduced by O. Witt, ascribe the function of the colouring basic derivatives of triphenylmethane to the presence of a quinonimide group. Rosenstiehl, on the contrary, ascribes the tinctorial function of these compounds to the para-positions occupied by the groups $Ar_2(R = H, CH_3C_2H_3 \ldots)$, to the central methanic carbon; and second to the union to this same methanic carbon of an element or a group of a function opposite to that of the group introduced into the benzenic nuclei. The only conclusion which the authors have been able to draw is that the hydrochlorates of the tinctorial matters of the amidotriphenylmethane group are not dissociated, whilst the ammonium chlorides and the nitrosodimethylaniline hydrochlorate are so most distinctly.

The Academy proceeded to nominate a foreign associate, *vice* the late Herr Kummer. Herr Weierstrass was elected with a majority of 43 votes, as against Professors Frankland and Huxley, who received each one vote.

E. Carvallo addressed a letter concerning a "sealed paper" concerning the theoretic establishment of the laws of theoretic absorption, and announced the early production of a memoir on the subject.

Dr. L. L. de Koninck addressed to the Academy a reclamation of priority concerning the properties of nickel and cobalt sulphides.

Reduction of the Congelation-point of very Dilute Solutions.—A. Leduc.—This paper does not admit of useful abstraction.

On a Sensitive Pressomètre (!) for Measuring the Pressures of Liquids.—Paul Charpentier.—This memoir requires the accompanying figure.

Measurement of the Intensity of Light by the Chemical Action produced. Experiments with Mixtures of Ferric Choride and Oxalic Acid.—Georges Lemoine.—The decomposition by light of mixtures of oxalic acid and of ferric chloride (*C. R.*, cxii.) may be utilised for measuring the luminous intensity; the greater it is found, the more rapid is the chemical transformation. The author finds that the heat liberated does not in reality disturb the results, and that the decompositions cease immediately on the suspension of the light. The natural light of the sun in summer, passing through a stratum of solution of potassium chromate of 25 m.m. in diameter varied in intensity from 0·001 to 0·007. If passed through blue glass, and through a layer of 25 m.m. of a solution of copper sulphate it was 0·40 to 0·50.

Certain Compounds of Lead Iodide with other Metallic or Organic Iodides.—A. Mosnier.—But few of the compounds formed by lead iodide with the metallic and the organic iodides are hitherto known. The author has obtained a double lead and ammonium iodide, $3PbI_2,4NH_4I,6H_2O$. Lead iodide forms double iodides with the tetramethylammonium, the tetraethylammonium, and phenylammonium iodides. The double sodium iodide obtained by the author has the composition $2NaIPbI_2,4H_2O$, whilst there crystallises out from the mother-liquor another compound, $2NaIPbI_26H_2O$. The double iodides of lead and lithium, and those of lead and the alkaline-earthy metals, and of the magnesium series, have also been obtained and examined.

Some Compounds of the Nitric Oxides with the Iron Chlorides.—V. Thomas.—On passing nitric oxide through a solution of ferric chloride at the ordinary temperature there is obtained a compound, Fe_2Cl_6NO; if the same experiment is conducted at 60°, there is produced $2Fe_2Cl_6NO$ as a red powder. A compound, $FeCl_2NO + 2H_2O$, is obtained in black crystalline needles. Another compound, $FeCl_2NO$, forms small yellow crystals.

Action of Formic Aldehyd upon Hydroxylamine Hydrochlorate and Monomethylamine Hydrochlorate.—A. Brochet and R. Cambier.—This paper does not admit of useful abstraction.

The Active Amylic Ethers.—Ph. A. Guye and L. Chavanne.—The authors arrange their results in four tables.

MISCELLANEOUS.

The John Scott Legacy and Premium.—We learn that Messrs. Cross and Bevan and Clayton Beadle, of London, have been awarded the John Scott Legacy Medal and Premium, by the Franklin Institute, for their "Discovery of a new Plastic Compound of Cellulose."

The Chemical Laboratory of Wiesbaden.—In the Winter Term 1894-95 there were fifty-six students on the books. Of these, thirty-three were from Germany, four from England, four from North America, three from Norway, three from Holland, two from Switzerland, one from Italia, one from Austria, one from Belgium, one from Sweden, one from Denmark, one from Russia, and one from Australia. 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. Leng, and Architect T. Brahm. The next Summer Term begins the 24th of April. 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.

Camera Club Photographic Conference, 1895.—The 1895 Conference will be held at the Camera Club, Charing Cross Road, on Tuesday and Wednesday, April 2nd and 3rd, under the Presidency of Captain W. de W. Abney, C.B., R.E., D.C.L., F.R.S., P.R.A.S.

On Tuesday, April 2nd, at 4 p.m., the President will open the Conference at the Club, and Papers will be read from 4 to 6 p.m. At 8 p.m. the Conference will be continued, and Papers will be read from 8 to 10 p.m.

On Wednesday, April 3rd, at 4 p.m., the Conference will be renewed, and Papers will be read from 4 to 6 p.m. At 8 p.m. the Conference will be continued and Papers will be read from 8 to 10 p.m.

On Thursday, April 4th, at 7.30 p.m., the Annual Dinner for Members and Friends will be held.

On Monday, April 8th, a Lantern Slide Exhibition will be given at the Society of Arts (by kind permission of the Council), and for this special tickets will be required.

The Members' Annual Exhibition of Photographs will be commenced at the Club on the first day of the Conference. A complete programme will be issued later and distributed. Visitors are cordially invited to take part in the discussions. Tickets of admission may be obtained through any Member of the Club, or on written application to the Secretary.

Recognition of Arsenic in Textile Goods, &c., in Sweden.—According to the Swedish law (April 10th, 1885) the sale of the following articles is forbidden:—Paper-hangings, curtains, carpets, Venetian blinds, artificial flowers, and other wares printed or painted from water-colours (glue, gum, starch, dextrine, albumen, &c.) with arsenical pigments, if from 200 square centimetres of the object a brown or black-brown arsenical spot can be obtained which is at least partially opaque. The arsenical spot is to be produced by the reduction of arsenic sulphide with potassium cyanide and sodium carbonate. and the reduction tube must have an internal diameter of $1\frac{1}{2}$ to 2 m.m. The same law holds good for tissues, yarns, lamp-screens, sealing-wax, wafers, stearine, or other candles; if in case of tissues and lamp-screens 100 square centimetres, and in case of other articles 21 grms., yield an arsenical mirror. According to the decree, in the report on the percentage of arsenic in the goods the weight or surface of the article used for investigation is to be mentioned, and there must be enclosed along with the arsenical mirror a piece of the tissue examined of at least 500 square centimetres on which all the colours present are represented. The tube enclosing the arsenical mirror must be melted at both ends. Both the specimen of the tissue and the arsenical mirror are to be sealed to the report or to a paper bearing the name of the analyst, and a number which is quoted in the report. The execution of the analysis according to the agreement of the Swedish commercial analysts is to be as follows:—A flask of the capacity of about 300 c.c. is connected with an open receiver by means of a 50 c.c. pipette, bent twice at a right angle, first upwards and then downwards. The receiver contains about 100 c.c., and is half filled with water, into which the point of the pipette dips slightly. The sample is placed in the flask along with 2 grms. non-arseniferous ferrous sulphate, and covered with 50 to 80 c.c. of concentrated hydrochloric acid free from arsenic, of sp. gr. 1·18 to 1·19. In case of bronze colours or other metallic articles there are added from 2 to 3 grms. of ferric chloride free from arsenic. The flask is heated and the hydrochloric acid is kept in ebullition as long as the pipette can be grasped with the hands. The distillate obtained is mixed with 50 c.c. of saturated sulphuretted hydrogen water, and diluted with 50 c.c. of water, and hydrogen sulphide is introduced. The arsenic sulphide deposited is allowed to stand for twelve hours, filtered through a small filter, washed until free from an acid reaction, and then dissolved in 5 c.c. of dilute ammonia (1 vol. ammonia of sp. gr. 0·96 and 1 vol. of water). The solution after the addition of 0·02 grm. sodium carbonate is evaporated to dryness on a watch-glass, the residue ground up with 0·3 grm. of a mixture of dry sodium carbonate and potassium cyanide, and reduced in a non-arsenical bulb tube in a current of carbonic acid. The bulb tube is so constructed that the narrow part in which the arsenical mirror is to be deposited joins close to the bulb of 2 centimetres in diameter.—*Zeitschrift fur Analyt. Chemie*, 1895, p. 88., and *Kemiska Notiser*.

MEETINGS FOR THE WEEK.

Monday, 18th.—Society of Arts, 4. (Cantor Lectures). "Commercial Fibres," by Dr. D. Morris.

Tuesday, 19th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8.. "Practical Carpet Designing," by Alexander Millar.

Wednesday, 20th.—Society of Arts, 8. "The Progress of the Abattoir System in England," by H. F. Lester.
— Geological, 8.
— Meteorological, 8.
— Microscopical, 8.

Thursday, 21st.—Royal, 4 30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Three Periods of 17th Century History—III. The Restoration," by Samuel Rawson Gardiner. M,A.
— Chemical, 8. "Studies in Isomeric Change—III. The Ethylbenzenesulphonic Acids," by Dr. G. T. Moody. "Some Oxypyridine Derivatives," by Miss Sedgwick and Dr. Collie. "Colouring Principle of *Toddalia aculeata* and *Evodia meliæfolia*," by A. G. Perkin and J. J. Hummel.

Friday, 22nd.—Royal Institution, 9. "Emily Brontë," by Sir Wemyss Reid, LL.D.
— Physical, 5. (At the Royal College of Science, South Kensington). "Objective Reality of Combination Tones," by Prof. A. W. Rücker, F.R.S., and Mr. Edser. "Some Acoustical Experiments," by Dr. C. V. Burton. "Use of an Iodine Voltameter," by Mr. Herroun.

Saturday, 23rd.—Royal Institution, 3. "Waves and Vibrations," by Lord Rayleigh, F.R.S.

A GUIDE TO STEREOCHEMISTRY, with an INDEX TO THE LITERATURE. By ARNOLD EILOART, Ph.D., B.Sc. (Lond.). Illustrated with Fifty Woodcuts and Five Plates. 8vo. 4s. post free. [1893.

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LECTURES.

Experimental Chemistry (Inorganic)	Prof. H. FRESENIUS, Ph.D.
Experimental Physics .. .. Stöchiometry	W. FRESENIUS, Ph.D.
Organic Chemistry..	E. HINTZ, Ph.D.
Chemical Technology	Prof. E. BORGMANN, Ph.D.
Microscopy, with exercises in Microscopic work	W. LENZ, Ph.D.
Chemistry and Analysis of Foods ..	Prof. H. FRESENIUS, Ph.D. Prof. E. BORGMANN, Ph.D. W. FRESENIUS, Ph.D., and E. HINTZ, Ph.D.
Hygiene .. .. Practical exercises in Bacteriology..	Dr. med. G. FRANK.
Technical Drawing, with exercises ..	J. BRAHM.

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL's Verlag, at Wiesbaden, or to the undersigned.

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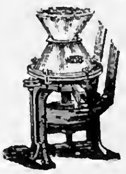

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THE CHEMICAL NEWS.

Vol. LXXI., No. 1843.

ARGON.

At the meeting of the French Académie des Sciences on Monday, March 11th, M. Berthelot announced that, having received from Dr. Ramsay a small specimsn of the new gas, he had submitted it to several experiments, and had found that it could enter into combination with certain organic compounds, especially with the vapour of benzene, under the influence of the silent electric discharge. He promised to publish next week the details of this experiment.

LIQUEFACTION OF HYDROGEN.

We learn that Professor Olszewski has liquefied hydrogen. Its critical point, measured with a platinum resistance thermometer, is −233° C., and its boiling-point at atmospheric pressure is −243.°

THE EXISTENCE OF AN ELEMENT WITHOUT VALENCY OF THE ATOMIC WEIGHT OF "ARGON" ANTICIPATED BEFORE THE DISCOVERY OF "ARGON" BY LORD RAYLEIGH AND PROF. RAMSAY.

By Lieut.-Col. SEDGWICK, late R.E.

The conclusion that inactive elements exist, or once existed, follows necessarily from the train of reasoning adopted by me in my book "Force as an Entity," published in 1890.

But before showing that my book contains a recorded anticipation of the existence of an element without valency of the atomic weight of "Argon," or rather of atoms of that kind, for the term Element seems to suggest the idea of something capable of combining, and I did not use it, I wish to make a few remarks in regard to the realistic view of Matter and Force, which enabled the existence of "Argon" to be thus, as it were, predicted.

The atoms are, of course, Newton's "solid massy hard impenetrable movable particles" of certain "sizes and figures," "so very hard as never to wear or break in pieces." And lines of force are viewed as Clerk-Maxwell viewed them in his paper "On Faraday's Lines of Force," though I was not aware that he had viewed them in that particular way when I wrote my book.

In that paper Clerk-Maxwell treats lines of force "not as mere lines, but as fine tubes of variable section carrying an incompressible fluid," and obtains supplies of the fluid by "sources where the fluid is created, and sinks where it is annihilated," and then gives mathematical investigations of some of the simplest problems in electricity and magnetism.

But in his paper "On Physical Lines of Force" he tells us that the conception he made use of was that of "currents in a fluid."

Now the view that lines of force are currents in an incompressible fluid is precisely the view taken in my book; but I have extended the fluid analogy so as to utilise the other fluid forms, namely, the pool, the film, and the wave.

By bringing matter in the form of atoms into the field to supply an "allurement" to which the fluid, with an overpowering tendency to attach itself to matter, will yield, so far as to overflow from its pools in fine streams upon atoms of matter, I am able to use pools as natural substitutes, both for the "sources" capable of creating the fluid from nothing, and for the "sinks" capable of annihilating it, with which Clerk-Maxwell worked and made his views unreal; and then I am able to proceed, for the fluid not only supplies by its currents a means of transporting atoms and bringing them together, but it also supplies by its films a binding material to bind atoms together in molecules, and molecules in masses, as shown by the binding power of a film of water between two clean sheets of glass and of water of crystallisation in a crystal.

If, then, we can get a form for the atom which will limit and define, in accordance with its valency, the ways in which other atoms can be bound on to it by films of the fluid, we shall plainly arrive at a natural and real explanation of chemical combination and valency.

Now, our ordinary every-day experience of the steadiness of things resting on flat surfaces, and of the unsteadiness of things resting on rounded surfaces, tells us that the form we are in search of is supplied by a sphere with flat places on its surface.

For we know that two bodies which are perfectly spherical in form cannot be united by a film, but will roll upon each other. If, however, the spheres have, both of them, large flat places on their surfaces, then they can be firmly united by a film by bringing their flat places together. And if one of the spheres has two such flat places on its surface, then two other spheres with flat places—and not more than two—can be united to it; or if it has three such flat places, then three other spheres with flat places—and not more than three—can be united to it; and so on.

By making the number of flat places correspond with valency, we get in the sphere with flat places on its surface an exact form for the valent atom. We also get, as a necessary consequence, a form for the non-valent atom, namely, that of a perfect sphere; and thus non-valent elements come in naturally and necessarily with this explanation.

But these are the precise views in regard to Force and Matter which are developed in "Force as an Entity." Chapter III. in that book deals with the form of the atom under the conception that the form of the valent atom is that of a chipped sphere with flat places on its surface corresponding in number to the valency of the atom, so that the monovalent atom has the form of a sphere with one flat place; a divalent that of a sphere with two flat places; a trivalent that of a sphere with three flat places; and a tetravalent that of a sphere with four flat places; and also that atoms in the form of perfect spheres can have no valency.

In that chapter it is shown in effect that the atomic weights of the whole of the metalloid elements afford most remarkable confirmation of the correctness of this view in respect of their hydrogen valency, since they run in series each of which contains a monovalent, a divalent, a trivalent, and a tetravalent member. And, moreover, these series are such that the atomic weights of all the members of a series can be obtained from the atomic weight of a single non-valent element, by cutting off from the atomic weight of the non-valent one portion weighing 2 to obtain the atomic weight of the monovalent, two portions weighing each 2 to obtain that of the divalent, three to obtain that of the trivalent, and four to obtain that of the tetravalent.

This is shown most remarkably by the first of these series, which runs thus:—

$$Fl^{I\cdot},\ 19;\ O^{II\cdot},\ 16;\ N^{III\cdot},\ 14;\ C^{IV\cdot},\ 12,$$

and is such that the atomic weights of all the members can be obtained in the way explained from a non-valent of atomic weight 20, as shown at pp. 60 and 61, of "Force as an Entity."

Thus $20-2\times1=18$ gives the atomic weight of the monovalent fluorine.
$20-2\times2=16$ that of the divalent oxygen.
$20-2\times3=14$ that of the trivalent nitrogen.
$20-2\times4=12$ that of the tetravalent carbon.

Now the atomic weights of all the members of this series plainly accord almost exactly with the view that they have atoms in the form of chipped spheres with one flat place in the case of the monovalent fluorine, two in that of the divalent oxygen, three in that of the trivalent nitrogen, and four in that of the tetravalent carbon, and that all are derived from a non-valent element with perfectly spherical atoms weighing each 20 by a process of chipping in which a portion weighing 2 is detached in making each flat place. For the monovalent fluorine atoms with one flat place ought in that case to weigh 18, the divalent oxygen atoms with two flat places 16, the trivalent nitrogen atoms 14, and the tetravalent carbon atoms 12; and these are their actual weights, in round numbers, with the exception only of the fluorine atom, the weight of which is 19 instead of 18.

In showing thus the correctness of our conclusions in regard to the form of the atom, we incidentally arrive at a determination of the atomic weight of one of the elements without valency, namely, of one of atomic weight 20, with atoms in the form of perfect spheres, with which we have all along been working, in the way shown at p. 61 of "Force as an Entity."

The three other metalloid series all point in the same direction, though not quite so satisfactorily as the first, and from them we can arrive in the same way at determinations of the atomic weights of three more elements without valency, and obtain the following values, viz., 37, 82, and 129.

This, too, is done in the Ideal and Real Tables and context at pp. 64 and 65 of "Force as an Entity," but the values obtained are not 37, 82, and 129, but 40, 80, and 120, in recognition of the closeness with which three, namely, 20, 37, and 82, out of the four values obtained in this way approximate to multiples of 20.

In this way, then, the existence of an element of atomic weight 40 having atoms in the form of perfect spheres, which are stated at the top of p. 66 to be "unaffected either by chemical affinity or cohesion," was determined from the series—

$$Cl^{I\cdot}, 35{\cdot}5;\ S^{II\cdot}, 32;\ P^{III\cdot}, 31;\ Si^{IV\cdot}, 28,$$

in connection with the other metalloid series, and the element tabulated in the Ideal Table at p. 64.

And thus an inactive element is tabulated, which agrees exactly with "argon," taking the atomic weight of argon in round numbers as 40.

It will be seen that though the determination of the atomic weight of this element without valency, which agrees exactly with argon, is only given incidentally, yet that the whole argument in connection with which it is given hangs upon the existence of elements without valency with atoms in the form of perfect spheres, and postulates the existence of such elements, though not necessarily in the present, because they may all have been converted by chipping into valent elements. Other considerations, however, come in to show the probability of the existence of such elements in the present day.

For we require in order to fill interstellar space a medium which, while transmitting gravitation, will offer little resistance to the motions of the heavenly bodies traversing it. And such a medium is supplied by elements without valency with the fluid with which we have been working, since, being unaffected by cohesion or chemical affinity, they will offer little resistance to the motions of the heavenly bodies while transmitting gravitation freely.

There was therefore not only a need for elements without valency in the past, but there is also a need for them in the present.

Accordingly the possibility that elements without valency, or rather the atoms of such elements, are in actual existence at the present day, and moreover that their atoms "are thickly distributed throughout space in the intervals between the heavenly bodies large and small," is pointed out at pp. 68 and 69 of "Force as an Entity."

"Force as an Entity" represents, however, only a preliminary statement of my conclusions, and at the same time a hurried statement because the inquiry was cut short by the expiration of the furlough which enabled it to be undertaken. It is therefore incomplete, and in many ways unsatisfactory.

I have since continued the investigation whenever time was available, and have obtained further results tending to improve and strengthen the case in every way.

I am now able to show in the same way that while the form of the metalloid atom is that of a sphere with flat places formed by cutting down the surface and thus reducing its weight, that of the metal atom is, on the other hand, a sphere with flat places formed by building up the surface, and thus making elevated flat places or flat-topped excrescences upon it, and adding to its weight.

Accordingly we have metal series showing gain in valency, attended with *gain* in atomic weight, corresponding exactly to the metalloid series, which show, as we have seen above, gain in valency, attended with *loss* in atomic weight.

Moreover we have both kinds of these series derived from the same element without valency in four cases, so that the metal series point just as strongly as the metalloid series to the existence of four elements without valency of atomic weights 20, 37, 82, and 130, in addition at least to four others of atomic weights 5, 62, 105, and 201 respectively.

These results were embodied by me in a paper which was sent to the Royal Society in November, 1892, and in another direction in the following December, and may perhaps be recollected by someone.

I am now able also to get over the difficulty arising from the marked difference between hydrogen and chlorine valency shown by some of the metalloid elements by pointing out that with large chlorine atoms abnormal valency may be expected to occur from molecules being caught and held without being regularly seated on flat places, and that the validity of this explanation is shown by the recognised fact that chlorine valency differs from hydrogen valency usually by molecules and not by simple atoms.

I have embodied these and other results of further investigation in another book which I had actually sent round to several publishing firms for consideration before the news of the discovery of argon reached me and rendered revision necessary.

3, Alexandra Road, Epsom,
March 15, 1895.

ABBREVIATED NAMES FOR CERTAIN CRYSTAL FORMS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

When the names of crystals have to be used constantly, as in lecturing upon or speaking about crystals and minerals, the waste of time involved by the present sesquipedalian names is a very serious matter, and it appears to me that it is desirable to shorten them somewhat. I therefore venture to propose the following curtailed names for certain crystals to be used ordinarily, although not always, in place of the descriptive terms now in use. It is not expected that these "short titles" will supersede

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* Read before the Aust. Assoc. for the Advancement of Science, Brisbane, January, 1895.

the older descriptive terms, but for conversational purposes they may prove useful.

The third column shows the number of letters saved in each case.

In every instance sufficient of the roots of the full name have been retained to indicate the source and meaning of the proposed abbreviated terms.

Abbreviated Names for Crystals.

Name.	Abbreviated name.	Saving of letters.
Octahedron	Octron	4
Hexahedron	Hexron	4
Rhombic dodecahedron	Rho-dodecron	8
Triakis octahedron	Tri-octron	8
Icositetrahedron	Icotetron or Icositetron	7 or 5
Tetrakishexahedron	Tetrahexron	7
Hexakisoctahedron	Hexoctron	8
Tetrahedron	Tetron	7
Trigonal-dodecahedron	Tri-dodecron	9
Deltoid-dodecahedron	Del-dodecron	8
Hexakistetrahedron	Hexatetron	8
Pentagonal-dodecahedron	Pentron or Pentadodecron	15 or 9
Trapezohedron	Trapezron	4
Tetragonal Pyramid	Tetramid	9
Ditetragonal Pyramid	Ditetramid	10
Tetragonal Prism	Tetrism	8
Ditetragonal Prism	Ditetrism	8
Sphenoid	Sphenoid	0
Scalenohedron	Scalenron	4
Hexagonal Pyramid	Hexamid	9
Dihexagonal Pyramid	Dihexamid	9
Hexagonal Prism	Hexism	8
Dihexagonal Prism	Dihexism	8
Rhombohedron	Rhomdron	4
	Total ..	174 or 166

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending February 28th, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 10th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 58 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 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, as far as possible, from Feb. 1st to Feb. 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.

Of the 58 samples examined one was recorded as "slightly turbid" and four as "clear but dull," the remainder were clear, bright, and well-filtered.

The unprecedented frost which visited the Thames valley during the month of February has prevented many samples being drawn for analysis, and it is difficult to make any fair comparison between the chemical composition of the waters during last month and the corresponding month last year, or with the months of December and January just preceding. It will therefore be sufficient to say that in every respect the freedom from pollution is of a very high character, the organic carbon and the brown constituent of the colour having diminished to about one-half the usual figures.

Bacteriological observations have been carried on during the whole of the month. Performing the operations in exactly the same manner as we have been accustomed to do them from the commencement, so as to admit of the results from month to month being strictly comparable among themselves, and keeping the culture plates incubating for 48 hours, the waters from the general wells have an average of 44 bacteria per cubic centimetre, that from the river at Hampton Court before filtration containing 7334.

Many localities in the South-east and East districts of London having had their service pipes frozen, the water from Aldgate pump was largely resorted to for domestic purposes. This has been for many years supplied from the New River Company, and it may interest consumers to know that analysis shows that the pump water is very pure, and is identical in composition with New River water from other localities. It was found to contain 133 microbes per cubic centimetre.

February has been a remarkably dry month. The rainfall (including snow) has only amounted to 0·21 inch, whereas the mean for the last twenty-five years for this month is 1·92, showing the large deficiency of 1·80 inch.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

SYNTHETIC EXPERIMENTS IN THE PYRAZOL SERIES.*

Part I.

By R. von ROTHENBURG.

L. Knorr, in a long series of brilliant experimental researches, has studied the oxygenated derivatives of pyrazol, as also those derived from phenylhydrazin, the pyrazolones, and pyrazolidones. In a series of short treatises in the Berlin *Berichte* I have given communications on the preparation of pyrazolon and its simplest derivatives, which I now give more fully in connection.

1. Pyrazolon is formed on the distillation of the calcium salt of (3)-carbon acid by oxidation of pyrazolidon, by means of the hydrazin hydrate from propiolic acid or its esters, from cumalic acid and β-aldoximacetic acid or their esters.

Pyrazolon forms a readily mobile liquid, turning yellow on exposure to light, and of very intense characteristic odour. It does not solidify in a freezing mixture, and boils at a pressure of 759 m.m. at 156—157°. It is very unstable in contact with concentrated hydrochloric acid, being completely decomposed at 100° into humoid substances, no hydrazin being split off. The ordinary organic solvents take it up very readily; even water dissolves it in appreciable quantity. Its specific gravity is 0·9137 at 16·5°. Its composition is $C_3H_4N_2O$. It dissolves in acids and alkalis, and forms salts with them. In the latter, pyrazolon passes doubtless into the form of an oxypyrazol.

The pyrazolon silver salt is precipitated from an ammo-

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* From the *Journal Praktische Chemie*.

niacal solution of pyrazolon as a white curdy precipitate, little sensitive to light, $C_3H_4N_2O,C_3H_3AgN_2O$. Other metallic salts precipitate the solution of pyrazolon, calcium, and barium chlorides white, copper sulphate a yellowish green, nickel sulphate an apple-green, and cobalt salts a peach-blossom. Platinum chloride throws down a very unstable yellow double salt.

(4)-Benzalpyrazolon is formed on boiling together equivalent quantities of pyrazolon and benzaldehyd. Its physical properties are very unpleasant. The semi-solid mass has a purple-red colour.

(4)-Isonitrosopyrazolon is obtained on passing nitrous acid (avoiding any excess) into a dilute alcoholic solution of pyrazolon. It and its following compounds have very intense colouration, especially if subsequently shaken out with ether, which shows a pure yellow or blood-red colour, and permits of (like the reaction with ferric chloride) the recognition of the smallest traces of pyrazolon in large volumes of liquid.

The nitroso-substance is strongly acid, and is easily or freely soluble in the ordinary solvents.

The pyrazolon-(4)-isonitro-silver salt is precipitated from the bluish red ammoniacal solution of isonitropyrazolon by silver nitrate (accurately neutralised) as a reddish yellow granular powder. It detonates if suddenly heated.

(4)-*p*-azotoluolpyrazolon is formed if a dilute solution of the para-diazotoluol salt is allowed to run into a feebly alkaline solution of pyrazolon, stirring well.

The new derivative crystallises from alcohol in small, splendid iridescent, purple-red leaflets, fusible at 219°. It is suitable for an approximate determination of pyrazolon in an aqueous solution. On reduction it behaves like a true azo-compound. Its composition is $C_{10}H_{10}N_4O$.

The (4)-azobenzenepyrazolon was obtained in an analogous manner as a well-crystallised substance, fusible at 185°.

Pyrazolon-(3)-carbon acid is formed on the saponification of its esters. The ethyl-ester is boiled for some time with concentrated hydrochloric acid until completely dissolved, the excess of acid is expelled by repeated evaporation with alcohol, and the substance is re-crystallised from dilute spirit. Its composition is $C_4H_4N_2O_3$. It forms two series of salts: neutral, in which only the carboxyl-group has a halogenous action, and basic, which have a (5)-oxypyrazol constitution.

The author describes the neutral, sodium, ammonium, and copper salts, and the basic pyrazolon-(3)-carbon, calcium, and silver salts, the latter of which has the composition $C_3H_2N_2OAg{\cdot}COOAg$.

(4)-Benzalpyrazolon-(3)-carbon acid is formed by heating the carbon acid for some hours with the calculated quantity of benzaldehyd to 120—130° in an oil-bath. It is sparingly soluble in ordinary solvents, but readily with a yellow colour in ammonia and alkalis. It separates from alcohol as a granular powder, fusible at 243°. Its composition is $C_{11}N_8N_3O_3$.

(4)-Isonitrosopyrazolon-(3)-carbon acid is best obtained by passing gaseous nitrous acid into the carbon acid washed up with alcohol, in which it dissolves with a deep red colour. The strongly acid nitroso-compound dissolves with a red colour in glacial acetic acid and caustic alkalis, but from ammonia with a violet colour. It crystallises from alcohol in golden yellow leaflets, which decompose at 215—219°. Its composition is $C_4H_3N_3O_4$.

The silver salt of the above acid,—

$$C_3H_2N_2ONOAgCOOAg,$$

is obtained by cautiously precipitating with a solution of silver nitrate the ammoniacal solution of the nitroso-compound previously mixed with solution of silver nitrate. It is an orange-red granular precipitate, which detonates slightly if heated.

Azobenzenepyrazolon-(3)-carbon acid, $C_{10}H_8N_4O_3$, is formed by running the calculated quantity of a diazobenzene salt into the alkaline solution of the carbon acid, refrigerating and stirring well. The colouring matter is very sparingly soluble, strongly acid, and forms a fiery-red granular powder, fusible above 250° with decomposition.

(To be continued).

THE CHEMOMETER.*

By W. OSTWALD.

If we bear in mind the general property belonging to every kind of energy, *i.e.*, that there is a certain magnitude (I call it, with Helm, intensity) the equality or inequality of which determines whether the energy in question is in equilibrium or not, we are led to a remarkable result as regards chemical energy. We must expect that, as there exist measuring-instruments for such magnitudes of intensity as temperature, pressure, and electric potential, which allow us to read off directly or indirectly the numerical value of these magnitudes, so there must be producible such a measuring-instrument for the intensity of chemical energy. Just as the thermometer enables us to determine directly for heat, the manometer for volume-energy, or the electrometer for electric energy, whether two regions on their immediate contact will be in thermic, mechanical, or electrical equilibrium, or not, there must be a "chemometer," by the application of which to two substances or complexes of matter we should ascertain whether chemical equilibrium exists between them or if a reaction would ensue when they are brought in contact.

In order to reply to the question whether such a chemometer exists or can exist, we must first consider the nature of chemical energy somewhat more thoroughly. But I may already remark that there is certainly hitherto no universal chemometer; but for a large class of chemical processes, including the most important, there is such a measuring-instrument which allows us to decide whether, and in what direction, a chemical action will ensue between two given substances.

Of course I am prepared to be told, on behalf of "pure chemistry," that we need nothing of the kind; we have simply to try. I must admit that I have as yet no conception of the possible practical application of the chemometer.

We have, in the first place, to take up the questions, What is chemical energy? and what are its factors?

The quantities of energy which are evolved or taken up in chemical phenomena, *i.e.*, in the transformation of given substances into others with different properties. It is presupposed that the energies do not change, or that such changes, if they occur, are taken into account.

We see, from this definition, that we must ascribe to the various substances determined quantities of chemical energy. According as the substances arising from a reaction contain more or less energy than the initial materials, energy is taken up or given off. These differences alone come to our knowledge; the absolute values of the chemical energy of each single substance are for us absolutely inaccessible.

Every form of energy may be resolved into two factors, which possess quite definite properties. The one, the factor of intensity, has its definite value for every portion of energy which is specially limited, and the equality of these values in two regions is the condition that on their combination the energy in question is in equilibrium; otherwise it passes from the territory of higher intensity to that of lower.

The second factor I have proposed to call capacity. It measures the quantity of energy which exists in the region in question and takes place in a given change of intensity. It in a general property of the magnitudes of capacity

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* From the *Zeitschrift fur Physikalische Chemie.*

that they follow the law of persistence in such a manner that in a defined structure through the boundaries of which energy neither enters nor escapes every magnitude of capacity retains its value unchanged. This proposition, single cases of which have long been known, has been of late advanced in a general form by Le Chatelier; it has an exception conditioned by the phenomena of thermic conduction and radiation, but which does not come into consideration for our further discussion.

What are these magnitudes in chemical energy? The factor of capacity is most easily recognised. The property of being preserved belongs in chemical processes to the quantities of matter, which must consequently be regarded as magnitudes of capacity. The magnitude of the intensity of chemical energy may then be defined as a quotient:—

$$\frac{\text{Energy}}{\text{Capacity.}}$$

It appears therefore as the work corresponding to the transfer of a given quantity of matter from one condition to another, divided by this quantity.

It is therefore not possible to determine values of chemical intensity absolutely, but only the differences of values for two defined conditions are accessible to measurement. It must also be emphasised that in this transfer all other energies must have intensities of constant value.

It will at once appear that the above determination of the value of chemical intensity, or of the chemical potential, as it was named by Villard Gibbs, agrees with the general definition of the magnitudes of intensity if we apply it to the question of equilibrium. Equilibrium presupposes equal intensities; whence it follows that for the unit of the quantity of matter on the transfer from one of the regions of equilibrium into the other, the work consumed or supplied must = O. This is in fact the definition of equilibrium.

After the factor of intensity of chemical energy has thus been recognised, the production of a "chemometer" seems to be merely a practical question like that of the thermometer after the concept of temperature had been decided. But if we seek to carry out the matter practically we encounter a peculiar difficulty which lies in the deficient comparability of chemical magnitudes. Here we must pause in order the better to survey the nature of the question.

Temperatures, masses, and many other magnitudes, are finally determined when we give their commercial value. Two temperatures the values of which (measured in equal units) are the same, are perfectly equal and differ in nothing. This simplicity of determination is met with in all magnitudes. For instance, electric potentials with the same numerical value are not necessarily equal, as they may have different signs (+ or −), and they require two determinations. Velocities, forces, magnitudes of motion, requires still more determinations.

(To be continued).

A NEW HYDROGEN SULPHIDE GENERATOR.

By J. I. D. HINDS.

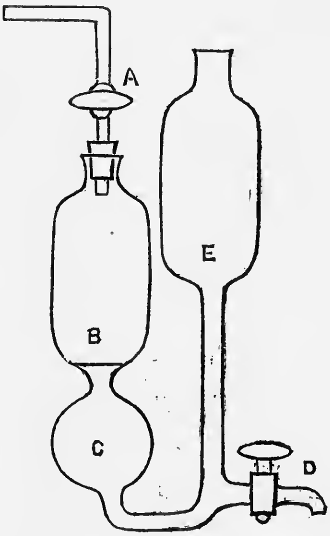
The accompanying figure shows a hydrogen sulphide generator in which objectionable features are reduced to a minimum, and the greatest convenience secured.

At B is a perforated disc of lead, glass, or porcelain, which supports the ferrous sulphide. When the stopcock at A is closed the acid is forced back by the gas into the vessel E. The globe C receives the gas, and prevents it bubbling back into E. When the acid is exhausted it is drawn off at D and a new supply added above.

The advantages of the apparatus are as follows:—

1. It is in one piece.
2. The pressure is small when the cock is closed.
3. The quantity of escaping gas is reduced to a minimum.
4. It is conveniently filled and emptied.
5. It is always ready.

The apparatus is furnished with a suitable support. It may be made of any size. The one now in use in the laboratory of Cumberland University has vessels and globe 8 c.m. in diameter. It was made for me by Messrs. Eimer and Amend, New York, and is giving entire satisfaction.



Cumberland University, Lebanon,
Tenn., U.S.A.

ON COMBUSTIONS.

By THOMAS T. P. BRUCE WARREN.

The determination of carbon and hydrogen in a substance where oxygen is estimated by difference admits of a degree of accuracy which, so far as hydrogen and oxygen are concerned, is simply marvellous, provided that ordinary care in manipulation is used.

In working with hydrocarbons containing sulphur, chlorine, bromine, and iodine, the estimation of hydrogen and carbon is not so satisfactory, nor so simple; we can make sure, with the first class of compounds, that every trace of moisture is removed from the tube and its contents before inserting the platinum boat with the material to be burnt.

Lead chromate cannot be dried in this way: hence moisture and dust, if present, cannot be got rid of; an element of uncertainty may arise if volatile compounds are produced, which sweep over the fused chromate, without being perfectly burnt.

Mixing in a combustion tube, powdered lead chromate with hydrocarbons of the second class by means of a wire is by no means satisfactory; add to this, that when a combustion is finished the tube cannot be used again, and the residual ash of the compound is lost, so that we cannot feel certain that all the carbon has been burnt. By combining the methods used for these two classes of hydrocarbons I obtain a degree of precision with the second class equal to that of the first class, and, what is of equal importance, the tube is left in a condition that it can be used several times without being re-packed.

Some previously ignited asbestos (long fibre) is picked to pieces and well dusted with finely.powdered lead chromate, which is loosely rammed into the tube.

A straight combustion-tube, 800 m.m. long, is packed as follows:—

A good-fitting cork which serves to keep out dust, and allows the materials to be added without the chance of falling out. Asbestos plug, about 80 m.m. long when well rammed down unto the cork. A tightly rolled-up copper-gauze cylinder, 25 m.m. long. Granulated copper oxide, 200 m.m. Copper-gauze cylinder, same as first, which keeps the oxide well together. A loose asbestos plug, 5 m.m. A loosely rolled-up plug of silver-foil, 25 m.m. Asbestos fibre, well dusted with finely-powdered lead chromate, 200 m.m., and which must not be too tightly rammed down. A plug of silver-foil, similar to the first, which prevents anything from falling into the platinum or porcelain boat, which occupies about 10 om.m. Plug of silver-foil, about 100 m.m. A good fitting cork. The corks can be bored when required, and the asbestos plug removed from the front part of the tube, some chemically clean copper turnings being inserted in its place, but only filling about one-half the space.

It is a good plan to keep a few tubes packed ready for use, omitting the boat and last silver plug.

To prepare the packed tube for use, and to make sure that it is not too tightly filled; replace the corks with perforated stoppers, either of cork or rubber; place in the furnace, and aspirate a current of dry air or oxygen, freed from CO_2, through the tube. Light the burners under that portion of the tube containing the copper cylinders and oxide, and, when it is well heated, turn on the other burners under the lead chromate and silver cylinders. The tube may be occasionally turned round, so as to ensure a gradual and uniform heating. After heating for one hour, and the copper oxide is fairly red-hot, the absorption-tubes are attached, after the prepared turnings are placed in the combustion-tubes; the stopcock of the aspirator is now adjusted for a very steady flow of air or oxygen. The joints are tested in the usual way.

The tared boat, containing 0·1 to 0·15 grm., is inserted, and also the following silver plug; the jets are opened under the boat and plug, and the combustion is allowed to proceed slowly.

A little of the substance is previously burnt off in a porcelain crucible, so as to become familiar with the colour and quantity of ash, and also to ascertain whether a platinum or porcelain boat would be preferable to use. Generally the carbon from the second class of compounds is much more difficult to burn than that from the first class. It is best to repeat the combustion until two consecutive results agree fairly well, and, as the same tube can be used over and over again, it is possible to finish four combustions, or even more, in a single day.

The copper turnings in the front part of the tube may be conveniently replaced by a plug of copper-gauze, provided it is left sufficiently bright to break up any oxides of nitrogen. To make sure whether nitrogen compounds are present, a preliminary test is made by fusing with metallic sodium or potassium in a test-tube, and examining the aqueous filtrate for cyanogen.

The same filtrate may be used to supply an approximation as to the sulphur and halogens present.

The mineral portion of the ash is examined in the usual way; it would clearly be wrong to trust only to what is left in the boat, as the volatile hydrocarbons may contain sulphur, halogens, nitrogen, oxygen, or certain metals,—which, of course, are carried away; metals which form volatile oxides, and are not arrested in passing over the lead chromate or copper oxide, will condense on the copper turnings in the front part of the tube, which, in such a case, must not be heated too strongly.

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.*

By AMOS PEASLEE BROWN.

(Continued from p. 132).

Action of 3 per cent Solution of Potassium Permanganate at Ordinary Temperature.

The conditions of this series of experiments were the same as those of the last. The tendency of the results to fluctuate instead of showing a gradual progression is now very marked. One of the one-hour pyrite oxidations shows more sulphur oxidised than is shown by any other individual result of the series. No explanation can be offered for such a discrepancy as this. On the other hand, the high result shown in the three-hour oxidation is quite easily explained by the marcasite having been little, if any, caked in this experiment. The two low results of pyrite three-hour and marcasite four-hour oxidations are readily explicable on the ground of caking of the material. As the barium sulphate was often determined several days after the oxidation was completed, it is obvious that no reliable notes could be made concerning the caking or non-caking of the mineral in the permanganate. With this strength of solution it is evident, too, that the main action of the permanganate is complete at the end of one hour, notably in the case of the marcasite, and it is only when very vigorous agitation exposes fresh surfaces of the mineral to the action of the $KMnO_4$ that any further action can take place. We therefore see that marcasite in one hour gives up as much sulphur as in five hours, and this is very graphically shown on Pl. xvii.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 3 per cent Solution of $KMnO_4$ at 22°.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with 3 per cent solution $KMnO_4$ cold	1·65	2·23	2·80	2·47	2·81
	(3·55)	2·31	(1·58)	2·62	2·28
Marcasite with 3 per cent solution $KMnO_4$ cold ..	2·72	2·17	2·87	2·88	2·83
	2·87	2·33	(3·31)	(1·89)	2·77

Action of 5 per cent Solution of Potassium Permanganate at Ordinary Temperature.

In this series, as in the last, the action, as far as pyrite was concerned, was practically complete at the expiration of the first hour, but in the case of the marcasite this point was not reached until probably the end of the second hour, and, in fact, in one case was progressive to the end. But one very great discrepancy is to be noted here in the three-hour column with marcasite. The low result in the next column is explained by caking.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 5 per cent Solution of $KMnO_4$ at 22°.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with 5 per cent solution $KMnO_4$ cold	2·39	3·03	3·22	2·89	2·79
	3·15	3·15	2·32	—	3·24
Marcasite with 5 per cent solution $KMnO_4$ cold ..	2·10	3·06	3·82	3·16	3·39
	2·52	3·76	(5·83) 2·77	(2·44)	4·17

This series finishes the experiments at ordinary temperatures. In all of them the action was comparatively slight, not exceeding at most 10 per cent of the contained sulphur in the mineral, which would not be sufficient to show any marked difference between the two minerals as bearing on their constitution, if the constitution which seems to be indicated by subsequent experiments (to be presently described) is the true one.

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* Read before the American Philosophical Society, May 18, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

The oxidations with potassium permanganate at a temperature of 100° were conducted by suspending the vessel containing the mineral and solution in boiling water. Both stoppered bottles and thin glass flasks closed with perforated corks were used for this series of experiments. The water was kept continually boiling, and the bottles or flasks were immersed deep enough to cover that portion of them containing the permanganate. Six or eight oxidations were made at one operation. The permanganate solution, after it had acted the required time, was treated as in the experiments conducted at ordinary temperatures described above. Much more active oxidation took place at this temperature (100°), but the tendency of the mineral to cake together was much more marked, and now this took place with pyrite as well as with marcasite. Moreover, the deposition of manganese dioxide in every case was now very great, causing often a stoppage of the oxidation until it could be dislodged. As these oxidation experiments had already occupied much time, only one trial was now made at each concentration of solution for each hour from one to five, unless, as before, marked discrepancies occurred, when two or more trials were made. The series of results are hence not so regular as they would have been had more trials been made, these irregularities arising from the difficulties that have been mentioned, as well as from the fact that the dilute solutions soon became exhausted, and that all solutions suffered some evaporation, but some more than others, causing irregular strength with the same solution. Nevertheless, the results agree in kind with those obtained at ordinary temperature, but differ widely in degree. Whereas at ordinary temperature the greatest amount of sulphur oxidised in marcasite by the five-hour trial with 5 per cent permanganate was 4·17 per cent, at 100° this became 16·36 per cent, or about four times as much.

Action of $\frac{1}{100}$ Normal Potassium Permanganate Solution at 100°.

The results given in the following Table show perhaps more strongly than either of the other series of experiments at 100° the effect of the different disturbing causes that have been mentioned. It especially shows the effect of caking of the pyrite, which now came in as an important disturbing factor. The result of this caking is shown in the three- and four-hour results with pyrite, both being very low. Marcasite, on the other hand, invariably caked and stuck to the bottom of the bottle, but as this was a constant source of error in this case, the results show a gradual and fairly even increase. Irregular results with marcasite were now largely conditioned by the evaporation of the solution or by the fact of whether the mineral was evenly caked over the inner surface of the vessel or concentrated in spots. The result of this latter way of caking will be better seen in some of the subsequent series of experiments.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a $\frac{1}{100}$ Normal Solution of $KMnO_4$ at 100° C.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with $\frac{1}{100}$ N. $KMnO_4$ at 100° C.	4·05	4·72	3·36	2·04	5·64
Marcasite with $\frac{1}{100}$ N. $KMnO_4$ at 100° C.. ..	3·17	3·84	3·76	5·63	5·61

(To be continued).

Royal Institution.—On Thursday next, March 28th, Dr. E. B. Tylor, F.R.S., will deliver the first of a course of two lectures at the Royal Institution on "Animism as Shown in the Religions of the Lower Races." The Friday Evening Discourse on March 29th will be delivered by Professor H. E. Armstrong, President of the Chemical Society. His subject will be "The Structure of the Sugars, and their Artificial Production."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 7th, 1895.

Dr. Armstrong, President, in the Chair.

Messrs. H. F. Stephenson, E. Joseph, H. L. Robinson, D. B. Butler, F. C. Sharrott, and J. A. Hatfield were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Prosper Henry Marsden, 47, Alma Road, Birkdale; Robert Selby Morrell, M.A., Ph.D., Gonville and Caius College, Cambridge; Frederick Gwilym Trehaine, Llyndirw, Llanishen, near Cardiff; Arthur William Warwick, Minah Mine, Wickes, Montana, U.S.A.

Notice was given of the following alterations in the by-laws proposed by the Council:—

In By-law I., at line 7, after the words "personally known" to strike out the remainder of the paragraph and substitute the following:—

"And the name of such Candidate shall be read at three ordinary scientific meetings, and such Certificate shall be published in full in the Society's *Proceedings*, and suspended in the Society's rooms or place of meeting, until the Candidate has been duly balloted for."

In By-law V., lines 2—4, to substitute the words "be two annual subscriptions in arrears," for the words "have left his subscriptions unpaid for two years, reckoning from the first of January preceding."

Of the following papers those marked * were read:—

*27. "*Dimethylketohexamethylene.*" By F. Stanley Kipping, Ph.D., D.Sc.

The oil obtained on distilling the calcium salt of αα'-αα'-dimethylpimelic acid with soda-lime (*Proc. Chem. Soc.*, 1892—93, 121—68) has been further investigated; the dimethylketohexamethylene which it contains has been isolated in a state of purity by acting on the fractionated product with hydroxylamine, separating the crystalline oxime thus produced, and decomposing it with hydrochloric acid.

Dimethylketohexamethylene is a colourless, mobile liquid boiling at 174—176°; it readily volatilises with steam, and has a very strong peppermint-like odour.

The oxime, $C_8H_{15}NO$ (found $C=68·03$, $H=10·76$; calc. $C=68·08$, $H=10·64$ per cent) crystallises from dilute alcohol in long needles melting at 114—115°; it has a strong smell very similar to that of camphor oxime.

When dimethylketohexamethylene is treated with warm, moderately concentrated nitric acid, it is rapidly attacked, but the first product of oxidation was not obtained in a crystalline condition; on prolonged boiling with nitric acid the ketone is converted into a crystalline substance, melting at 65—68°, the properties of which, as far as could be ascertained, are identical with those of the lactone of α-hydroxy-α-methylglutaric acid.

*28. "*The Use of Barium Thiosulphate in Standardising Iodine Solution.*" By R. T. Plimpton, Ph.D., and J. C. Chorley.

The authors find that barium thiosulphate, $BaS_2O_3H_2O$, prepared by precipitation from solutions of sodium thiosulphate and barium chloride, is well adapted to the titration of iodine solutions. The substance can easily be obtained pure, keeps well, and reacts readily with a solution of iodine, while the progress of the reaction is marked by the gradual disappearance of the crystals which are oxidised to soluble barium tetrathionate. An important advantage in the use of barium thiosulphate is its high molecular weight, 267 parts of the substance corresponding to 127 parts of iodine. 50 grms. of sodium thiosulphate and 40 grms. barium chloride are dissolved each in 300 c.c. of water, the warm solutions mixed, and the crystalline powder which soon separates collected, thoroughly washed with cold water, and dried at 30° C.

The precipitate has the composition $BaS_2O_3H_2O$, and would lose water if dried at a much higher temperature.

In performing the titration a weighed quantity of the powder is placed in a stoppered bottle and shaken with water; the iodine is run in until the thiosulphate is almost dissolved, starch solution is then added, and the process completed, care being taken to thoroughly shake the bottle after each addition of iodine.

29. "*The Melting-points of Racemic Modifications and of Optically Active Isomerides.*" By F. Stanley Kipping, Ph.D., D.Sc., and William J. Pope.

The melting-point of a racemic compound is, in almost all cases, different from that of its optically active isomerides; only a few substances are known of which the racemic and optically active isomerides have the same melting-point, and even in these cases it is by no means certain that the supposed racemic modification is not merely a mixture in equal proportions of the two isomerides of opposite optical sign.

During the investigation of π-monobromocamphor, we found the optically inactive form of this substance to be a true racemic compound, since it crystallises in an optically biaxial system, whilst its dextro-isomeride crystallises in the uniaxial tetragonal system; both racemic and active forms have the same melting-point, the two substances melting sharply at 93—94°. A series of determinations of the melting-points of various mixtures of these isomerides was made in order to ascertain the influence exerted on the point of fusion of the one by the other; this led to the somewhat remarkable result that, in spite of the difference in crystalline form, mixtures of the two substances, as well as the pure compounds themselves, melt at the same temperature, viz., 93—94°.

On examining the corresponding chloro-derivatives, we found that dextro-π-monochlorocamphor also melts at the same temperature as its inactive isomeride; further, the melting-point of mixtures of the two substances is always the same as that of the pure constituents. We cannot assert that the inactive modification of π-monochlorocamphor is a true racemic modification with the same certainty as in the case of the bromo-compound, the crystals of the former being very poorly developed and not suitable for crystallographic measurement.

The racemic nature of inactive π-monobromocamphor is, however, beyond all question, and we therefore conclude that it is possible for a true racemic compound not only to melt at the same temperature as its optically active isomeride, but also to have no effect on the melting-point of the latter when mixed with it. This behaviour is analogous to that of mixtures of two isomorphous substances for which the curve plotted between the molecular compositions and the melting-points is a straight line joining the melting-points of the two pure substances.

30. "*Phenyl Ethers of Methylene- and Ethylene-glycols. Synthesis of α-Methylbutyrolactone.*" By E. Haworth, B.Sc., and W. H. Perkin, jun., F.R.S.

These substances, which are required in the course of some synthetic experiments now in progress, were prepared as follows:—

Methyleneglycol diphenylether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$, is obtained when methylene chloride is digested in alcoholic solution with sodium phenate; it is a colourless, crystalline substance, which melts at 20°, and distils at 205° (50 m.m.).

Ethyleneglycol phenylether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is formed quantitatively when glycolchlorhydrin reacts with sodium phenate; it is a thick, colourless liquid, which boils at 165° (80 m.m.).

When ethylene bromide is digested with sodium phenate, *bromhydrin phenylether*, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2Br$, a colourless, crystalline mass, m. p. 32°, b. p. 144° (40 m.m.), is obtained with glycoldiphenylether,—

$$C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5.$$

colourless crystals, m. p. 96°.

Chlorhydrin phenylether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$, is obtained when ethylenechlorobromide, $Br{\cdot}CH_2{\cdot}CH_2Cl$, is digested with sodium phenate; it is a colourless, crystalline solid, which melts at 30°, and distils at 220°.

The preparation of α-methylbutyrolactone was conducted as follows:—

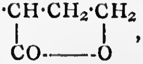
The sodium compound of ethylic methylmalonate was digested in alcoholic solution with bromyhdrin phenylether, and the resulting *ethylic γ-phenoxyethyl-α-methylmalonate*,—

$$(COOC_2H_5)_2{\cdot}C(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5,$$

a colourless liquid, b. p. 230° (45 m.m.), converted by hydrolysis into *γ-phenoxyethyl-α-methylmalonic acid*,—

$$(COOH)_2{\cdot}C(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5.$$

This crystalline acid, which melts at 125°, is decomposed on distillation into carbon dioxide and γ-phenoxyethyl-α-methylacetic acid (m. p. 77°); and this, by treatment with hydrobromic acid and subsequent digestion of the product with sodium carbonate solution, yields phenol and *α-methylbutyrolactone*,—



$$\begin{array}{l} CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_2 \\ \quad\ \ | \qquad\qquad | \\ \quad CO\text{——}O \end{array},$$

which is a colourless oil distilling at 201°.

31. "*Methyl Isobutyl Acetic Acid*,

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOH.$$

By W. H. Bentley, B.Sc., and M. W. Burrows, B.Sc.

This acid, which has not hitherto been described, was required for the purpose of comparing its properties with those of some fatty acids obtained by fusing camphoric acid with potash. The present paper deals with its preparation and properties.

Isobutyl bromide, $(CH_3)_2{\cdot}CH{\cdot}CH_2Br$, was heated with the sodium derivative of ethylic methyl malonate, the product being ethylic methylisobutyl malonate,—

$$(CH_3)_2{:}CH{\cdot}CH_2{\cdot}C(CH_3)(COOC_2H_5)_2,$$

distilling at 230—235°. This, on hydrolysis, yielded the corresponding dibasic acid—methylisobutylmalonic acid, $(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}C(CH_3)(COOH)_2$, which melts at 122°, and on distillation is decomposed, forming methylisobutylacetic acid, $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOH$. The pure acid boils at 204—205°, and in its properties resembles the other higher acids of the fatty series.

The following derivatives have been prepared in order to assist in its identification,—

Ethyl Salt, $C_6H_{13}{\cdot}COOC_2H_5$.—A colourless oil boiling at 165—166°.

Anilide, $C_6H_{13}{\cdot}CO{\cdot}NH{\cdot}C_6H_5$.—A colourless solid crystallising from petroleum in silky needles; m. p. 110°.

p-*Toluide*, $C_6H_{13}{\cdot}CO{\cdot}NH{\cdot}C_7H_7$.—A colourless solid melting at 86°.

Anniversary Meeting.

This meeting, at which the election of Officers and Council for the ensuing year will take place, will be held on Wednesday, March 27th, at 3 o'clock in the afternoon.

PHYSICAL SOCIETY.

Ordinary Meeting, March 8th, 1895.

Mr. Walter Baily, Vice-President, in the Chair.

Mr. Naber exhibited and shortly described "*A New Form of Gas Voltameter.*"

The chief advantages claimed for this instrument are that either the oxygen or the hydrogen can be collected separately, and that the level of the liquid inside and outside the burette can be made the same: thus no correction has to be applied to the volume of the gas on this account. Variations in the temperature and barometric pressure are allowed for by reading an air thermometer, which is fixed alongside the burette. The inventor considers that this instrument will compare favourably in accuracy with the copper and silver voltameters now in general use.

Prof. S. P. Thompson considered, that now so much care had been bestowed on the design of a gas voltameter, this instrument might come into more general use than heretofore.

Dr. Johnstone Stoney, F.R.S., exhibited—(1) "*The Local Heliostat*"; (2) "*An Improvement in Siderostats.*"

By a local heliostat the author means one which can only be used in plates the latitudes of which differ slightly from that of the place for which the instrument was specially constructed. The limits within which the instrument works with sufficient accuracy for ordinary spectroscopic work are such that one instrument can be used in any place in the British Isles. The heliostat exhibited was a modification of one previously described by the author, which is now in very general use, and it is capable of sending a reflected ray in any direction in, or nearly in, a horizontal plane. In the new instrument the pendulum clock, previously used to supply the motive power, is replaced by a balance-wheel clock; this change decreases the cost of the instrument, while it adds to its portability. A tangent screw, worked by a long rod, supplies a slow motion for adjusting the position of the reflected beam, and is of use when examining the spectra of the solar prominences, &c. The instrument is adjusted in the meridian by means of a gnomon and horizontal divided circle, which form a sundial. This divided circle is so arranged that it is always horizontal when the polar axis is in adjustment, and can therefore be used whatever the latitude of the station at which the observations are being made. In connection with the use of a heliostat in conjunction with a spectroscope, the author recommends, when using a grating, the introduction of a large glass prism between the heliostat and the slit of the spectrometer. An impure spectrum is thus formed on the slit, and, by moving the slit to the part of this spectrum corresponding to light of the wavelength under observation, the difficulties due to the overlapping of the spectra may be in a great measure overcome. After mentioning that the great difficulty in designing a siderostat which should work with "astronomical accuracy" is to get a form of sliding motion which should be free from back-lash and should move perfectly regularly, Dr. Stoney exhibited a model of a form of mechanism for obtaining such a motion, which he had devised. The principle on which the instrument depends is that, if you have a point fixed to a circle which rolls on the inside of another circle of double the diameter, this point will describe a straight line. The smaller disc does not, in the model exhibited, roll directly on the larger disc, but an idle wheel is introduced which rolls on the *outside* of both the discs. Slip is avoided by placing steel bands between the idle wheel and the discs, one end of each of the two bands being fixed to the circumference of the idle wheel, while the other ends are fixed one to the circumference of each of the disks. Back-lash is prevented by means of a spiral spring attached to a point in the smaller disc, this point being so chosen that it moves nearly perpendicularly to the direction in which the spring acts. Hence the spring is always stretched to nearly the same amount, and no extra strain is brought to bear on the driving clock in different portions of the instrument.

Prof. S. P. Thompson considered that the best method to employ when using sun-light was to incline the telescope, &c., parallel to the polar axis, under which circumstance the mirror of the heliostat need only rotate about a vertical axis.

A paper "*On a Simple Form of Harmonic Analysis*" was read by Mr. G. U. Yule.

At a former meeting of the Society Prof. Henrici showed a form of analyser in which the paper on which the curve is traced was given a to-and-fro movement, a planimeter being used as an integrator. The author, being struck with the advantages of the use of a planimeter both as regards cheapness and simplicity, has devised another form of analyser, in which a planimeter is used. The principle on which this instrument works is as follows: — Suppose we have a straight line (XX) which can move parallel to the base line of the given curve, so that every point in this line describes a perpendicular to the base. Further, suppose that a disc, the circumference of which is some aliquot part of the base of the curve,—say $2\,l/n$ where $2\,l$ is the base length, is capable of rolling on the line (XX) without slip. If the centre of the disc is brouget over the initial point of the curve, and any point (D) at a distance r from the centre on a horizontal diameter is marked; then, if the centre of the disc is made to describe the curve which is to be analysed, the area of the curve described by the point D is given by the equation—

$$R_1 = a + \cos n\,\pi.\,\frac{r\,n\,\pi}{l}\int_{-l}^{+l} y \sin n\,\theta.d\,x,$$

where a is the area of the curve to be analysed. Similarly, if the point D is taken originally on a vertical diameter, the area of the curve swept out is—

$$R_2 = a + \cos n\,\pi.\,\frac{r\,n\,\pi}{l}\int_{-l}^{+l} y \cos n\,\theta.d\,x.$$

In any practical case it is convenient to take r some multiple of $1/\pi$ units of length, say 10; then the above equations become—

$$R_1 = a + \cos n\,\pi.10\,n\,B_n$$

and

$$R_2 = a + \cos n\,\pi.10\,n\,A_n,$$

where B_n and A_n are the coefficients of sin $n\,\theta$ and cos n. in the Fourier series expressing the equation to the curveθ The areas of the curves traced out by the point D (R_1 and R_2) are obtained by allowing the tracing-point on an Amsler planimeter to rest in a small conical hole at D. The line XX is the edge of a rolling parallel ruler, which has a rack cut along it. A series of toothed wheels give the coefficients of the different terms in the series. In the instrument exhibited there were wheels to give the first four terms, but the author said it was possible to work with wheels which gave the sixth term. The above analyser was the outcome of a simple step-by-step integrator which the author had devised. In this case the base line of the curve, having been divided into a number of equal parts, then by means of a scale of sines attached to the instrument, the tracing-point of a planimeter is set at a point whose abscissæ is sin $n\ \theta$, while it is moved parallel to the axis of y through a distance, $\delta\,y$ corresponding to one of the elements into which the base was divided.

Prof. Henrici said he had at one time considered the question of constructing an analyser which should employ a planimeter as the integrator, and he was particularly pleased with the instruments exhibited. Since the area required was the difference between the area of the original curve which is traced out by the centre of the disc (K) and the curve traced out by the point D, and since this area is really the area swept out by the straight line KD, if we attach an integrating wheel to the disc with its axle parallel to KD, the required area can be directly obtained from the reading on this wheel. In addition, if a second integrating wheel were fixed to the disc with its axle perpendicular to KD, the coefficients of cos $n\,\theta$ and sin $n\,\theta$ could be both obtained by going round the curve once. The instrument devised by Mr. Yule was practically the inverse of one he (Prof. Henrici) had invented.

Dr. Burton pointed out some incorrect signs in the proof given. These, however, do not affect the final expressions obtained.

Mr. Inwards suggested that errors due to back-lash might be avoided by using either a double wheel or a double rack, so that by means of a spring each side of the teeth which were engaged might be in contact at the same time.

Prof. Minchin gave a short account of a paper by Mr. H. N. Allen, entitled "*The Energy Movements in the Medium Separating Electrified or Gravitating Particles.*"

The object of the paper is to trace out the equi-potential surfaces and lines of flow for two electrified points or gravitating particles, and then to consider the paths along which the "energy cells" move when the charged points or gravitating particles either move towards or away from one another. By energy cell the author understands the small volume of the dielectric bounded by the walls of a tube of force and by two neighbouring equi-potential surfaces, which can be looked upon as containing a certain definite amount of energy. The author gives two figures showing the paths of the energy cells (1) when the changed particles come together and meet, (2) when they separate and move off to infinity in opposite directions. Using Maxwell's expression for the pressure along the lines of force and the equal tension at right angles required by his theory to account for the attraction exerted by the sun on the earth, the author has calculated the energy density in the medium at the surface of the sun. The value obtained is 16 horse-power hours per c.c. Hence he concludes that at a distance from all gravitating bodies a c.c. of ether contains at least this amount of energy. Prof. Minchin showed how, by the use of polar co-ordinates, the expressions given by the author could be simplified. He also gave a graphical method of obtaining the equi-potential surfaces for any configuration, having given those for any other configuration. He pointed out that by a similar line of reasoning to that used by the author, the energy per c.c. of the medium at the surface of Arcturus must be 8100 times as great as at the surface of the sun, so that the minor limit given above by the author must be multiplied by 8100 at least.

NOTICES OF BOOKS.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali, with the Collateral Branches. By George Lunge, Ph.D., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich (formerly Manager of the Tyne Alkali Works, South Shields). Second Edition, Revised and Enlarged. Vol. II. London: Gurney and Jackson (Successors to Mr. Van Voorst). Large 8vo., Pp. 930. 1895.

This work, in its entirety, may almost be characterised as an encyclopedia of the "heavy" chemical manufactures. The author, in his introduction to the volume now before us, remarks that though the Leblanc process will probably not survive to a remote future, it is still "necessary to describe it, both because it is sure to be carried on for a considerable further period, and because its fundamental operations are typical for alkali-making, and also generally for other branches of chemical industry."

Dr. Lunge begins with an account of the properties and occurrence in nature of the raw materials and products of the alkali industry.

On the occurrence of common salt in nature we find some highly interesting details. The common salt of Cheshire, a district mentioned as the seat of the greatest salt industry in the world, is stated as containing only 98·250 per cent of natural NaCl. Many commercial qualities contain as little as 95 per cent, whilst some of the samples obtained from the Astrachan salt lakes contain as much as 99 per cent. The yearly average home production in Britain exceeds two million tons, and the exportation is now only 700,000 tons. The production in India is given as about one million tons, though in the north-western provinces and in Affghanistan it might be indefinitely increased.

Little as it is now regarded, sodium sulphate occurs in various parts of the world, even in commercial quantities. Near Tiflis there is a bed of very pure Glauber's salt of a thickness of from 5 to 10 feet.

No important natural source of hydrochloric acid is known, which, considering its action on the animal organism, is not to be regretted. The author rightly asserts that factory air should in no case ever contain more than 0·01 per cent HCl. As in the previous line he has stated that "a strong man found air with 0·005 per cent HCl unbearable," we suspect an error in printing, 0·001 per cent seems more likely. It is interesting that of old the three expressions natron, kali, and soda meant the same thing, fixed alkali of any kind. The word "soda" is used by Geber. Hence the Germans have scant justification for retaining the name natron in place of soda. The natural deposits of sodium carbonate—urao, trona—are not unlikely to affect the alkali markets of the world. But where soda occurs in soils, in streams, or lakes in quantities not admitting of collection, it is a serious evil, as being ruinous to vegetation.

The second chapter gives directions for the analysis of the raw materials and the products of the soda industry. The examination of hydrochloric acid is considered at some length, as some possible impurities are much objected to by consumers—a subject to which Dr. Lunge returns elsewhere.

In speaking of the analysis of soda-ash, the author complains that German manufacturers titrate their samples without previous filtration, thus calculating any calcium carbonate as soda. As a standard acid he prefers the hydrochloric to the sulphuric.

As the only indicators needing consideration, he mentions litmus and methyl-orange. Litmus, when properly purified, he considers "hardly less sensitive than methyl-orange." Here we must advise a comparison with Reinitzer's papers on volumetric analysis, a translation of which has appeared in the Chemical News (vol. lxxi., p. 31). Dr. Lunge further gives a caution against the use of tropæolin OO instead of methyl-orange.

The degrees showing the strength or values of soda-ash receive an interesting notice. The English degrees signify the percentage of real or available soda, Na_2O; German degrees show the percentage of sodium carbonate; and French degrees show merely the arbitrary standard of Descroizille.

The French system is very justifiably pronounced the most irrational. The German system quotes as carbonate any other sodium salts which act upon the test acid. Thus they may return a sample of caustic soda as containing 120 per cent or upwards.

The English system was made ridiculous by the conduct of certain analysts acting on behalf of the Liverpool brokers. They insisted on taking the equivalent of soda as = 32 instead of 31, and were thus able to assert that a soda-ash of 50 per cent actual Na_2O should be valued as = 51·6 degrees. Ill fared any work's chemist who refused to make himself a party to this fraud (see Chemical News, vol. xxxii., pp. 267, 280, 302; also xxxiii., 8, 17, 31, 40). The practice was even defended as late as 1884, in *Journal Soc. Chem. Ind.*, pp. 17, 19, 63, 214, 311. Dr. Lunge was even severely attacked for having exposed this absurdity in the first edition of the present work. It was at one time possible to make a good profit by buying soda on the Tyne test and selling it again, nominally at the same price, on the Liverpool test!

The determination of the specific gravity of a soda-ash is of some importance. The denser qualities cost less in freight, and are preferable in all fusings and igniting operations. Sodium sulphate was formerly present in a Leblanc soda as 8 to 10 per cent. Now it is reduced to 0·3 to 1 per cent, whilst in ammonia-soda it may be 0·1 or even less. On the other hand, undecomposed common salt is present in the best Leblanc soda as 0·25 to 0·5 per cent, whilst in the ammonia-sodas it ranges from 0·5 to 2·5 per cent.

Sodium carbonate present in caustic sodas is in some cases not merely useless, but positively injurious. Hence the German trade custom refuses to calculate the carbonate present in caustic as available soda.

Passing over Chapters III., IV., V., VI., not as being as less value, but simply as a question of space, we come to the consideration of the hydrochloric acid produced in the manufacture of salt-cake. At the present day hydrochloric acid no longer counts as a by-product, but is often the main source of profit in the Leblanc process.

The use of lofty chimneys for carrying off the gaseous hydrochloric acid was found to be a very costly failure. A list is here given—on the authority of the Belgian Commission of 1855—showing the comparative sensitiveness of trees to the vapour. The hornbeam is placed as the most sensitive and the grey alder as the most resistant. According to our own observations, the walnut is the most sensitive and the plane the most resistant.

Dr. Lunge does not omit to expose the vulgar error o "smoke consumption." The more completely a ton of coal or coke is consumed the more completely is all its sulphur converted into sulphurous or sulphuric acid. He reminds us that chemical works are often blamed for injury to vegetation which may be chiefly or entirely due to the smoke from domestic chimneys, iron and steel works, &c. He also shows that even at Widnes human health is little affected by hydrochloric acid vapours.

We shall early return to a further notice of this invaluable work.

CORRESPONDENCE.

OERTLING'S BALANCES.

To the Editor of the Chemical News.

Sir,—Kindly note that the balances illustrated in Messrs. Elliott Bros.' Catalogue of January 1st, 1895, are those made by me, though, by inadvertence, in the catalogue Messrs. Elliott Brothers' name appears on the illustrations instead of mine.

Messrs. Elliott Brothers have most courteously undertaken to call attention to this mistake in the copies of the catalogue still in their possession.—I am, &c.,

L. Oertling.

Turnmill Street, London, E.C.,
March 19, 1895.

ARGON.

To the Editor of the Chemical News.

Sir,—I am unaware if the following suggestion has been made, so will ask, Might not argon, this indifferent member of the chemical family, be induced to marry carbon, as nitrogen does when presented to carbon and potash at a red heat? In other words, are argon analogues of KCu and $K_4Fe_2Cy_6$ obtainable?—I am, &c.,

Philip Holland.

London, March 19.

A DISCLAIMER.

To the Editor of the Chemical News.

Sir,—I shall be very greatly obliged if you will allow me to take the earliest opportunity of stating in the Chemical News, as the paper most representative of all the different branches of the chemical profession, that the production appearing in the current number of a journal called *Tit-Bits*, under the title of "A Chemical Analyst and His Work," purporting to be an account of myself and of an interview with me, has been written and published without my knowledge or consent. Its appearance has given me extreme annoyance, and I have addressed to the Editor of the journal a strong representation on the subject (which I hope will appear in the next issue), as well as to the contributor: the latter a friend and past pupil, who, without giving me the faintest hint beforehand of his intention, or asking my permission, has made use of materials gleaned in the course of a purely private conversation, during an ordinary visit from himself, such as he had paid me on several previous occasions.

I should not have dreamed of consenting to the publication of what I regarded as nothing more than confidential chat between two friends. Of course I accept no responsibility for any portion of the account in question; which, moreover, in various respects is distorted and inaccurate.

I thoroughly believe that the contributor's motives were the kindliest; but I have never met with a more forcible example of the application of the saw, "Save me from my friends."

The very first intimation I received that such an article had been written was in a letter from my friend on the morning after the paper was issued from the press.—I am, &c.,

E. Godwin Clayton.

43 and 44, Holborn Viaduct, E.C.,
March 16, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 9, March 4, 1895.

Notice of the Life and Work of Admiral Paris (of the Section of Geography and Navigation).—E. Guyon.—This extensive memoir contains nothing which can be noticed in the Chemical News, though we must appreciate the tact with which M. Guyon avoids political allusions.

Prophylactic Treatment of Swamp Fevers.—M. d'Abbadie.—The author, on the faith of experience, recommends a daily fumigation of the naked body with sulphur as a preservative against the intermittent or pernicious fevers of tropical climates. (The agent, of course, will not be sulphurous acid, but sulphur volatilised in its free state).

The Month of February at the Observatory of the Parc Saint Maur.—E. Renou.—To find as low a mean temperature for February we have to go back to 1740 and consult the observations made by Réaumur.

Oxides and Sulphides with Acid and Basic Functions. Zinc Sulphide.—A. Villiers.—This paper will be inserted in full.

Calorimetric Researches on Saline Solutions. Sodium Acetate.—E. Morney.—The author represents his results by a curve taking as abscissæ the concentrations and as ordinates the heats of dilution. The curve constructed at 15 is almost rectilinear from the concentration 0 to 10 and ascends rapidly. Then there appears a very decided curvature between the concentrations 5 and 17·5. Above this latter concentration the curve tends to become asymptotic to a right line parallel to the axis of the abscissæ the ordinate of which will be nearly equal to 18.

On Hexamethylene-Amine; Salts of Ammonium; Action of Acids; Production of Primary Amines.—M. Delépine.—This paper does not admit of useful abridgment, and can scarcely merit insertion in full.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., No. 23, 1894.

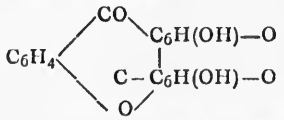
Researches on the Basic Nitrates.—M. Athanasesco.—It is known that the solutions of a great number of basic sulphates if heated in sealed tubes to temperatures varying according to the character of the metal give rise to a basic sulphate more or less crystalline. The author has applied the same process to other metals, and has obtained a basic copper nitrate of the composition $NO_3.H,2CuO,3H_2O$.

Method of Preparing Paraquinones by means of Indophenols.—The author pulverises finely 10 grms. of the indophenol corresponding to the quinone to be obtained. He places the powder in a flask with a long neck, pours in 50 grms. of water, agitates, and drops in gradually 20 grms. pure sulphuric acid. The flask is closed with a stopper having a slight notch at the side, and shaken up again. The reaction is quickly effected. The liquid is then allowed to cool and exhausted with ether. The ethereal solution is transferred to a 1-litre flask, and evaporated by means of a current of air. After the evaporation of the ether, the flask is connected, on the one hand, with a refrigerator and a cooled receiver, and on the other with a flask giving off watery vapour. The steam carries off the quinone, which is found pure in the receiver.

On a New Quinone. Ethylbenzoquinone.—H. P. Bayrac.—The new compound takes the form of brilliant laminæ of a gold-yellow, or, on crystallisation from ether, of long prismatic needles. It has a powerful irritating odour. It melts at 38·2°, dissolves very sparingly in cold water, much more readily in hot water; it is very soluble in ether, but slightly less so in alcohol. It contains—Carbon, 70·33; hydrogen, 5·78; Oxygen, 23·89 per cent.

On a Series of Indophenols. General Method of Preparation.—H. P. Bayrac.—Already inserted.

Constitution of Ceruleine.—Maurice Prudhomme.—Ceruleine contains two hydroxyls, and its constitution may be represented as follows:—



Quinine Chlorhydrosulphate.—Charles Lepierre.—This salt is destined to play a great part in therapeutics, especially for hypodermic injections.

Determination of the Total Nitrogen in Urine by Henninger's Method.—H. P. Bayrac.—A dispute concerning a modification of the Kjeldahl method, which in reality was introduced in 1884 by Henninger, and not, as Moreigne supposes, by Petit and Monfet.

Royal Institution.—The following are the Lecture Arrangements after Easter:—Professor George Forbes, three lectures on "Alternating and Interrupted Electric Currents"; Professor E. Ray Lankester, four lectures on "Thirty Years Progress in Biological Science"; Professor Dewar, four lectures on "The Liquefaction of Gases"; Dr. William Huggins, three lectures on "The Instruments and Methods of Spectroscopic Astronomy" (the Tyndall Lectures); Mr. Arnold Dolmetsch, three lectures on "Music and Musical Instruments of the Sixteenth, Seventeenth, and Eighteenth Centuries"—(1) English, (2) French, (3) Italian (with Illustrations upon Original Instruments); Mr. Seymour Lucas, two lectures on "Picture Making"; Professor Edward Dowden, two lectures on "Elizabethian Literature"—(1) The Pastoral, (2) The Masque. The Friday Evening Meetings will be resumed on April 26th, when a Discourse will be given by Dr. John Hopkinson, on "The Effects of Electric Currents in Iron on its Magnetisation; succeeding Discourses will probably be given by The Earl of Rosse, Veterinary Captain Frederick Smith, The Hon. G. N. Curzon, M.P., Professor Walter Raleigh, Mr. J. Viriamu Jones, Professor Alfred Cornu, and other gentlemen.

MEETINGS FOR THE WEEK.

Monday, 25th.—Society of Arts, 4. (Cantor Lectures). "Commercial Fibres," by Dr. D. Morris.
— Medical, 7.
Tuesday, 26th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
— Institute of Civil Engineers, 8.
Wednesday, 27th.—Society of Arts, 8. "Modern Photogravure Methods," by Horace Wilmer.
— British Astronomical Association, 5.
— Chemical, 3. Anniversary Meeting. Anniversary Dinner, Hotel Metropole, 7.
Thursday, 23th.—Society of Arts, 4.30. "Chitral and the States of the Hindu Kash," by Capt. F. E. Younghusband.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Animism, as shown in the Religions of the Lower Races," by E. B. Tylor, F.R.S.
Friday, 29th.—Royal Institution, 9. "The Structure of the Sugars and their Artificial Production," by Prof. H. E. Armstrong, F.R.S.
Saturday, 30th.—Royal Institution, 3. "Waves and Vibrations," by Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS.
Vol. LXXI., No. 1844.

DISCOVERY OF HELIUM.*

By Prof. W. RAMSAY, F.R.S.

In seeking a clue to compounds of argon I was led to repeat experiments of Hillebrand on clèveite, which, as is known, when boiled with weak sulphuric acid, gives off a gas hitherto supposed to be nitrogen. This gas proved to be almost free from nitrogen; its spectrum in a Plücker's tube showed all the prominent argon lines, and, in addition, a brilliant line close to, but not coinciding with, the D lines of sodium. There are, moreover, a number of other lines, of which one in the green-blue is especially prominent. Atmospheric argon shows, besides, three lines in the violet which are not to be seen, or, if present, are excessively feeble, in the spectrum of the gas from clèveite. This suggests that atmospheric argon contains, besides argon, some other gas which has as yet not been separated, and which may possibly account for the anomalous position of argon in its numerical relations with other elements.

Not having a spectroscope with which accurate measurements can be made, I sent a tube of the gas to Mr. Crookes, who has identified the yellow line with that of the solar element to which the name "helium" has been given. He has kindly undertaken to make an exhaustive study of its spectrum.

I have obtained a considerable quantity of this mixture, and hope soon to be able to report concerning its properties. A determination of its density promises to be of great interest.

THE SPECTRUM OF THE GAS FROM CLÈVEITE.†

By WILLIAM CROOKES, F.R.S.

By the kindness of Professor Ramsay I have been enabled to examine spectroscopically two Plücker tubes filled with some of the gas obtained from the rare mineral clèveite.‡ The nitrogen had been removed by "sparking." On looking at the spectrum, by far the most prominent line was seen to be a brilliant yellow one apparently occupying the position of the sodium lines. Examination with high powers showed, however, that the line remained rigorously single when the sodium lines would be widely separated. On throwing sodium light into the spectroscope simultaneously with that from the new gas, the spectrum of the latter was seen to consist almost entirely of a bright yellow line, a little to the more refrangible side of the sodium lines, and separated from them by a space a little wider than twice that separating the two sodium components from one another. It appeared as bright and as sharp as D_1 and D_2. Careful measurements gave its wave-length 587·45; the wave-lengths of the sodium lines being, D_1 589·51, and D_2 588·91. The differences are therefore—

	Wave-lengths.	Differences.
D_1	589·51	
		0·60
D_2	588·91	
		1·46
New line.. ..	587·45	

The spectrum of the gas is, therefore, that of the hypothetical element helium, or D_3, the wave-length of which is given by Angstrom as 587·49, and by Cornu as 587·46.

Besides the helium line, traces of the more prominent lines of argon were seen.

Comparing the visible spectrum of the new gas with the band and line spectrum of nitrogen, they are almost identical at the red and blue end, but there is a broad space in the green where they differ entirely. The helium tube shows lines in the following positions:—

		Wave-length.		
(a)	D_3, yellow	587·45	Very strong.	Sharp.
(b)	Yellowish green ..	568·05	Faint.	Sharp.
(c)	Yellowish green ..	566·41	Very faint.	Sharp.
(d)	Green	516·12	Faint.	Sharp.
(e)	Greenish blue	500·81	Faint.	Sharp.
(f)	Blue	480·63	Faint.	Sharp.

I have taken photographs of the spectrum given by the helium tube. At first glance the ultra-violet part of the spectrum looks like the band spectrum of nitrogen, but closer examination shows considerable differences. Some of the lines and bands in the nitrogen spectrum are absent in that from the helium tube, whilst there are many fine lines in the latter which are absent in nitrogen. Accurate measurements of these lines are being taken.

ATTEMPTS TO MAKE ARGON ENTER INTO CHEMICAL COMBINATION.*

By M. BERTHELOT.

Towards the end of the month of February I received from Dr. W. Ramsay some argon contained in a tube arranged for spectrum analysis, and in a small bulb or cylinder sealed at each end before the blowpipe. Dr. Ramsay at the same time wrote me a letter, in which he kindly gave the following information:—The gas "had been circulated in the apparatus for the absorption of nitrogen, until the nitrogen bands disappeared and there was no more contraction. The density of the specimen was 19·95, hydrogen being 1, and the relation between the specific heats 1·64."

It has been with this specimen, guaranteed by Dr. Ramsay, that I have made the following experiments. The gas in the cylinder was removed by immersing it in a vessel of mercury, breaking off the two ends successively, and collecting the gas directly in a small pipette. Its volume was 37 c.c.

The idea which prompted my experiments is the following:—I endeavoured to bring about the combination of argon with other elements under the influence of the silent electric discharge. This discharge is, indeed, much more effectual than the spark, because it more effectually secures the permanence of instable compounds; the effect of the silent discharge being too rapid to cause the subsequent destruction of the products owing to a sensible duration of a high temperature, a circumstance which is opposite in the case of the spark. Nitrogen, for instance, in the presence of hydrocarbon gases or vapours gives rise to most varied products of condensation under the influence of the silent discharge—products which decompose with elevation of temperature; whilst under the influence of the spark only one compound, hydrocyanic acid, is formed, and were this compound not stable at a high temperature nothing would be formed. Carbonic oxide condenses under the influence of the silent discharge, whilst it is almost unaltered by the spark. Again, the silent discharge, acting on a mixture of nitrogen and hydrogen, can produce several percentages of ammonia, while the spark only gives infinitesimal quan-

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* A Paper communicated to the Chemical Society at their Anniversary Meeting, March 27, 1895.

† A Paper communicated to the Chemical Society at their Anniversary Meeting, March 27, 1895.

‡ Clèveite is a variety of uraninite, chiefly a uranate of uranyle, lead, and the rare earths. It contains about 13 per cent of the rare earths, and about 2·5 per cent of a gas said to be nitrogen.

* *Comptes Rendus*, cxx., No. 11, p. 581, March 18, 1895.

tities. Under the influence of the silent discharge, nitrogen is absorbed by water, with formation of nitrite of ammonia, a compound which is decomposed on standing, and spontaneously at the ordinary temperature.

It was therefore necessary to study the action of the silent discharge on the combination of argon with oxygen, hydrogen, and the hydrocarbons. As the quantity of gas at my disposal was small, I tried first the hydrocarbons which lend themselves better to this form of experiment.

I exposed argon to the action of the silent discharge under the conditions described in my "Essai de Mechanique Chimique" (t. ii., pp. 362, 363), which are those of the silent discharge with variable potential, regulated by Ruhmkorff's apparatus, with a vibrating conductor and high tension. The apparatus employed is described and figured in the *Annales de Chimie et de Physique*, 5e serie, t. x., pp. 79, 76, 77, figs. 5, 2, and 3 (1877). It allows removals and accurate measurements. It was under such conditions that I succeeded in causing free nitrogen to be rapidly absorbed by hydrocarbons, hydrates of carbon, and the most diverse organic matters (" Essai de Mechanique Chimique," t. ii., p. 384).

Argon appears to be equally absorbed, as I shall explain, although with more difficulty. I have especially worked in the presence of vapour of benzene, which is very effective in the case of nitrogen. The action of the silent discharge on the mixture is accompanied with a faint violet glow, visible in darkness. On one occasion, out of five experiments, there was formed at the end of some time a fluorescent body, which gave out a magnificent greenish light and a special spectrum; but the quantities of matter at my disposal were too small to allow me to seek for the conditions necessary to produce these effects.

These are the data of a careful experiment, effected on 10 c.c. of argon. One hundred volumes of gas from Dr. Ramsay were measured, put into contact with some drops of benzene—this increased the volume of the gas about one-twentieth,—and then introduced into the discharge-tube, into which a trace of liquid had entered. The electricity was then allowed to act, with relatively moderate tensions, for ten hours. The total gaseous volume was reduced about a tenth. The vapour of benzene was absorbed by a drop of concentrated sulphuric acid, with the usual precautions, and the volume of the residue was measured; it was reduced to 89 volumes, showing 11 per cent of diminution.

This volume was again mixed with benzene vapour, and the experiment was re-commenced, employing much higher tensions; the volume diminished rapidly. At the end of three hours, all corrections being made, the volume was only 64; that is to say, it had experienced a fresh reduction of 25 per cent.

What remained was again mixed with benzene and submitted a third time to the silent discharge, using strong tensions, for several hours. There was then found a crude gaseous residue measuring 32 volumes after making all corrections. But this residue was not pure argon; it contained nearly half of combustible gases, products of the reaction of the discharge on the benzene. According to eudiometric analysis, these 32 volumes contained—

Hydrogen	13·5
Benzene vapour	1·5
Argon	17·0

It contained no alkaline vapour.

To sum up, of 100 volumes of argon, benzene successively condensed 83 in the state of chemical combination produced by the silent discharge; that is to say, five-sixths. The dimensions of my apparatus would not allow me to go beyond that.

The products of this combination represent too small a weight to permit of a detailed examination. I will only say that they resemble those produced by the silent discharge acting on nitrogen mixed with the vapour of benzene; that is to say, they consist of a yellow, resinous, odorous matter condensed on the surface of the two glass tubes between which the electric action is exerted. This substance, submitted to the action of heat, decomposes, forming volatile products, and leaving a bulky carbonaceous residue. The volatile products of decomposition turn litmus paper blue; this indicates that an alkali is formed in the decomposition. But it was not possible to examine it more closely for want of material. In any case, the conditions under which argon is condensed by hydrocarbons tend to assimilate it still closer to nitrogen.

Let me here observe that if it is permitted to raise the molecular weight of argon to 42 instead of 40—an increase which the limits of error in the experiments hitherto made, in which numbers as high as 51·2 have been obtained, do not entirely exclude—this weight would represent one and a half times that of nitrogen; that is to say, argon would bear to nitrogen the same proportion that ozone does to ordinary oxygen,* with this fundamental difference, that argon and nitrogen are not transformable the one into the other; not otherwise than the isomeric or polymeric metals. But I do not wish to insist on such conjectural correspondences.

In any case, the inactivity of argon ceases under the circumstances I have described. When more considerable quantities of argon are available, it will doubtless be easy by the ordinary methods of chemists to take these first combinations or any other analogous ones realisable with oxygen, hydrogen, or water as the starting-point of transformations, and to obtain the normal series of more simple compounds. There is also room for the search for the presence of compounds of argon in organised beings.

CRYSTALLISED CARBON DIOXIDE.†

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

When solid carbon dioxide is examined under the microscope, it presents along its edges projecting wire-like crystals which have branching filaments issuing from them apparently at right angles, resembling somewhat the groups of minute crystals seen in crystallised iron, gold, and ammonium chloride.

The rapidity with which the carbon dioxide evaporates makes it difficult to catch the form of the crystals, either by photography or other means.

COMBUSTIONS WITH LEAD CHROMATE.

By THOMAS T. P. BRUCE WARREN.

In packing a combustion tube with copper oxide and lead chromate, as given in a previous communication (Chem. News, lxxi., p. 144), I recommended to insert an asbestos plug between the second copper gauze prism and the first silver foil prism, with the view of preventing any dust of copper oxide reaching the lead chromate. I have since found that by repeated handling some copper oxide gets to the chromate, and in time a little copper chloride is formed, and although the silver prism arrests it, there is just the chance that some may be carried over to the absorption tubes.

If much chlorine is present, it is preferable to omit the copper oxide and to replace it with lead chromate dusted on asbestos.

To make sure that every trace of moisture is removed, heat the tube and asbestos to redness, attach the absorption tubes and aspirate a gentle current of dry oxygen or

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* Or, better still, the proportion which the camphenes, $C_{10}H_{16}$, bear to the sesquiterebenes, $C_{15}H_{24}$.

† Read before the Aust. Assoc. for the Advancement of Science, Brisbane, January, 1895.

air freed from CO_2 for about one hour; if the weight is unaltered, allow the tube to cool down, insert the boat and substance, and proceed with the combustion.

SYNTHETIC EXPERIMENTS IN THE PYRAZOL SERIES.*

Part I.

By R. von ROTHENBURG.

(Continued from p. 142).

Pyrazolon-(3)-carbonic acid-(4)-orthobenzoïc acid is formed like the foregoing if orthodiazobenzoïc acid is used in place of the diazobenzene salts. It has more decided acid properties, and is distinguished from the former by its greater solubility. It crystallises from dilute alcohol in red needles. Melting-point 227°.

Pyrazolon-(3)-carbonic methylester.—Obtained from hydrazin hydrate and oxalaceticmethylester. It forms yellow crystals, fusible at 226·5—227·5°. Its composition is $C_5H_6N_2O_3$.

(4)-Benzalpyrazolon-(3)-carbonic methylester is obtained from the ester by heating with equimolecular quantities of benzaldehyd to 120—130°. Sparingly soluble in all solvents; forming a yellowish brown powder, which undergoes no change up to 250°.

(4)-Isonitrosopyrazolon-(3)-carbonic methylester.—This compound dissolves in alcohol, glacial acetic acid, and alkalis with a deep red colour, but in ammonia with a violet-blue. It separates from dilute alcohol or acetic acid in yellowish red warty crystals melting at 199—201°, and has rather strongly acid properties.

Pyrazolon-(3)-carbonic ethylester is formed from oxalic-acetic or acetylendicarbonic diethylester by adding gradually hydrazin hydrate to oxalacetic ester, diluted with 4 or 5 parts of alcohol, when heat is liberated spontaneously. It is then heated to ebullition for thirty minutes, and allowed to cool, when the entire quantity of pyrazolon-(3)-carbonyl hydrazin, insoluble in alcohol, is separated out. The alcohol is distilled off, and poured hot into a capsule; the mass congeals; it is drained, washed in ether, and crystallised from ether-alcohol in flat needles; it is soluble in alcohol, almost without limit, sparingly soluble in benzene and ether, freely in methylic and amylic alcohol. It melts at 179°. Its composition is $C_6H_8N_2O_3$.

(4)-Benzalpyrazolon-(3)-carbonic ester is a reddish yellow granular powder sparingly soluble in all solvents, and having the composition $C_{13}H_{12}N_2O_2$.

(4)-Isonitrosopyrazolon-(3)-carbonic ethylester is obtained by passing gaseous nitrous acid into the alcoholic solution of the ester. It is easily soluble in organic solvents, and dissolves in alkalis with a deep red, but in ammonia with a violet-blue. From alcohol it crystallises in yellow, acid, granular crystals, fusible at 182°, and of the composition $C_6H_7N_3O_4$.

(4)-Azobenzenepyrazolon-(3)-carbonic ethylester consists of $C_{12}H_{12}N_4O_3$.

Pyrazolon-(3)-carbonic ethylester (4)-ortho-azobenzoïc acid crystallises from alcohol in fiery red needles, fusible at 255°.

Pyrazolon-(3)-carbonamid.—Best obtained from methyl ester and concentrated alcoholic ammonia on heating in a tube to 100—120°. Sparingly soluble in ordinary solvents, and crystallises from water in granular masses; fusible at 219° with decomposition. Well-crystallised derivatives are also obtained from aniline, toluidine, anisidine, phenetidine, naphthylamine, and phenylhydrazine.

Pyrazolon-(3)-carbonylhydrazin has the composition $C_4H_6N_4O_2$. Sparingly soluble in all organic solvents. Crystallises from water in flat needles, fusible at 238—239°.

Pyrazolon-(3)-carbonyl-benzalhydrazin crystallises in fine needles associated in flocks, and decomposed above 250°.

(4)-Benzalpyrazolon-(3)-carbonal-benzyl-hydrazin.—A yellowish red powder, very sparingly soluble in all ordinary solvents, and unchanged at 250°.

(4)-Hydropyrazolon-(3)-carbonyl-hydrazin. If hydrazin-hydrate in excess is allowed to act upon an alcoholic solution of (4)-isonitroso-pyrazolon-(3)-carbon ester, this compound separates as a fiery red precipitate, very sparingly soluble. It is very interesting, since it dissolves with a red colour in alkalis, like the azo derivatives of diazo-salts, and displays on reduction the properties of a true diazo-compound. It dissolves in acids with a yellow-red colour, and is unchanged at 250°.

(4)-Benzalazipyrazolon (3)-carbonyl-benzal-hydrazin proves that the hydrazonhydrazid has retained its nature as a hydrazin derivative. On shaking with benzaldehyd suspended in water the fiery red compound passes into a lemon-yellow derivative, melting at 217·5°.

Pyrazolon-(3)-aldehyd.—A yellow oil, easily re-converted by oxidation into the carbon-acid.

(3)-Dipyrazolonketon is contained in the less volatile fractions of the distillation of pyrazon-carbon acid with lime. It passes over at 202—203°, and shows the characteristic pyrazolon reactions. Its composition is $C_7H_6N_4O_2$.

(3)-Diparazolon-methylenphenylhydrazin is obtained on heating the alcoholic solution of the ketone with phenylhydrazin. It gives the characteristic reactions of the pyrazolones, dissolves readily in organic media, and separates from alcohol in flocks; fusible at 113°.

(To be continued).

EXPERIMENTS ON THE SPONTANEOUS HEATING OF FATTY OILS DIFFUSED IN FIBROUS OR POROUS SUBSTANCES.

By Dr. RICH. KISSLING.

The author had the opportunity of studying a case of spontaneous combustion which was checked at its outset. A cask of boiled linseed oil in a warehouse had been leaking on the previous day, and the leakage had been absorbed in sawdust. This sawdust was put in an iron pail, and left in the warehouse all night. About midnight the watchman observed an empyreumatic odour, and saw a slight smoke rising from the pail, which became a flame, when the pail with its contents was carried into the open air. The fire was quenched before the contents had been too much altered by the heat. There can be no doubt that the ignition was spontaneous. The warehouse was lighted electrically, and no matches were ever introduced.

On a careful experimental examination it was found that on passing a current of dry air through raw linseed oil (previously heated to 100°), it gained daily 0·87 per cent of its weight of the absorption of oxygen. The total increase of weight was 0·41 per cent, and there had been a loss of 0·46 per cent from the escape of volatile matter—acids of the methane series.

If the surface of contact between the fatty oils and the air, and if external refrigeration is prevented, a considerable rise of heat is produced by the process of oxidation, which under favourable circumstances may extend to an actual ignition of the fibrous matter.

The quantity of heat liberated by the spontaneous oxidation of the oil depends:—(*a*) on the chemical nature of the oil concerned, *i. e.*, on its affinity for oxygen; (*b*) on the size of the surface of contact between the oil and the air, *i. e.*, on the mechanical texture of the fibrous or other porous matter, as well as on the relative proportion of

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* From the *Journal Praktische Chemie.*

the oil and such fibrous matter; (*c*) on protection against external refrigeration; and (*d*) on the action of light.

On these conditions it may be remarked, under (*a*), that the behaviour of different oils varies greatly; with rape oil the rise of temperature was not recognisable; with cotton oil it was very trifling; with raw linseed oil stronger; and with boiled oil very considerable. The fibrous substances examined (*b*) differed likewise. The greatest liberation of heat took place with silk fibres; then followed wool, cotton, jute, and lastly hemp. (*c*). The protection against refrigeration is of importance, as the tendency of oils to become oxidised with a liberation of heat rises with the temperature. (*d*) The action of light is similar to that of heat.

The activity of micro-organisms in these processes of oxidation is unimportant.—*Zeitschrift Angewandte Chem.*, Jan. 15, 1895.

(Dr. Kissling omits to state whether the silk fibre used in his experiments was pure or "loaded." The latter article has occasioned serious fires).

THE CHEMOMETER.*

By W. OSTWALD.

(Continued from p. 143).

Such simplicity of determination is not common to all magnitudes. Electric potentials, *e.g.*, are not necessarily equal when their numerical values are alike, as they may have a different sign; they therefore require two determinations. Velocities, forces, quantities of motion, require still more determinations.

Two forces, numerically equal, may differ in sign and in direction, and to determine the direction we require the three cosines of direction in reference to any given system of axes. But all these magnitudes have always a finite number of determining elements by means of which they may be respectively converted.

But the factors of chemical energy are even devoid of this mutual relation. They differ from each other in infinitely many respects. Thus oxygen and iron have no direct relation to each other. We have no means of converting one *grm.* of iron into so and so many grms. of oxygen, or of replacing it by oxygen of an equal value, whilst the values which we have just considered may always be transformed into others of the same kind. And what relates to the capacities of chemical energy must necessarily hold good for the intensities, as the latter are defined by the former.

The only kind of relations which is possible among the chemical factors of energy is expressed by the equations of chemical reaction. When we write—

$$\text{Iron} + \text{Oxygen} = \text{Iron Oxide},$$

we say that there exists between iron and oxygen no direct or mutual relation of conversion; but there exists a relation between the three substances, iron, oxygen, and iron oxide, such that the third can be made from the two former, and, inversely, that iron and oxygen can be produced from iron oxide. The customary expression, that iron oxide *consists* of iron and oxygen, is brief but inaccurate. For in iron oxide we find neither the properties of iron nor those of oxygen; and if we say that, though the attributes of both substances disappear they are still substantially present, we only need to attempt to connect clear and definite conceptions with this expression; the result will be infallibly such that we desist from any further attempt in this direction. Indeed the chemist of the present day becomes so early familiar with the atomic hypothesis (certainly very convenient as a means of instruction) that no doubt suggests itself to him as to the reality of the atoms and their continued existence in compounds. But in an enquiry of a general character it becomes so much the more necessary to separate carefully matter of fact from what is merely hypothetical, in order to have solid ground for our superstructures.

From these considerations we infer that the capacities of chemical energy do not possess, like all other capacities, a common measure, but that they can be reduced to so many mutually independent kinds as there exist so-called elements. Between these elements there exists a relation only in so far that many of them can act upon each other in such a manner that there may arise new substances, and consequently new capacities, which, however, are no longer independent, but have such a relation to the elements that they may be regarded as the sum of the latter. These relations are further subject to the known stœchiometric laws, that of constant proportions, of multiple proportions, and of combining weights. In addition, there is the above-mentioned law of the maintenance of the species, according to which a transition from one element to another is impossible.

The corresponding intensities of chemical energy are subject to exactly the same limitations. Hence, also, there are about seventy kinds which cannot in any manner be referred to each other, and the existing relations between the elements and the chemical compounds obey the stœchiometrical laws.

If we therefore suppose a "chemometer" really executed in manner above mentioned, we cannot be satisfied with a single instrument. We must have at least seventy such appliances independent of each other, one for each element, and should have no means of comparing the indications of the oxygen chemometer with those of the apparatus for hydrogen.

According to these considerations the especial characteristics of chemical energy seem entirely to cut off the possibility of producing such apparatus of a general character. For manometers, electrometers, thermometers, are possible only because all pressures, electric potentials, temperatures, &c., are alike in their nature and the relation of any two individual values of this kind can be fully expressed by a number.

On further reflection, however, the matter does not appear hopeless. Certainly an absolute, universal chemometer is not possible. Still for many cases the intensity of chemical energy may be expressed in a comparable measure, independent of the factors of chemical energy display, in reference to each other, this great number of irreducible cases. This may be effected by the employment of such kinds of energy as are inseparably connected with chemical processes, and the most suitable energy for this purpose seems to be the electrical.

According to Faraday's law, the far-reaching significance of which has only become manifest in our days, in many chemical reactions, especially those in which electrolytes are concerned, there are manifested electrical processes which are proportional to the chemical reactions and are inseparably connected with them. The connection is such that the capacities of electrical energy, the quantities of electricity, are proportional to the capacities of the chemical energy, the quantities of substance, and in different substances the quantity of electricity combined with quantities chemically equivalent, is always the same.

(To be continued).

Rotatory Power of Isomeric Ethers in the Amylic Series.—Ph. A. Guye.—From the author's polariscopic experiments, executed under conditions as comparable as possible, it results that among the amylic derivatives the propyl group is more active than the isopropyl group, and the latter, again, more than the butyl group.—*Bull. de la Soc. Chim. de Paris*, xi.-xii., No. 23.

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* From the *Zeitschrift fur Physikalische Chemie.*

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.*

By AMOS PEASLEE BROWN.

(Continued from p. 132).

Action of 1 per cent Potassium Permanganate Solution at 100°.

The results of the oxidation shown in this series are chiefly remarkable as still further illustrating the action of the solution on the caked material, as shown in the four- and five-hour trials with pyrite and the four-hour trial with marcasite. This latter shows, too, the effect of having the caked mineral massed in one spot. With this exception, the marcasite oxidations are progressive and fairly uniform (the two-hour trial falls somewhat below what it doubtless should be), but the pyrite shows a sharp fall in the four- and five-hour trials. The cause of this has been indicated. That the concentration of the solution by evaporation caused an increase in the action seems to be indicated by the result of the five-hour marcasite oxidation, but this is much more strongly marked in the 5 per cent series in the case of pyrite, which will be referred to later on.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 1 per cent Solution of $KMnO_4$ at 100°.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with 1 p. c. $KMnO_4$ at 100° C.	6·03	6·98	8·38	6·11	6·88
Marcasite with 1 per cent $KMnO_4$ at 100° C. ..	6·43	5·61 6·25	8·56	7·40	9·10

Action of 3 per cent Solution of Potassium Permanganate at 100° C.

The average results of this series of oxidations were very good, with the exception of two members of the series—the marcasite five-hour trial and the pyrite three-hour. This latter was repeated, but with a similar low result. Leaving these two out of account, the average results show a very fairly even rate of progression, which have been brought out in the diagram (Pl. xvii.). It is evident from an inspection of the following table that the marcasite oxidations of the four- and five-hour trials were arrested by some disturbing influence.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 3 per cent Solution of $KMnO_4$ at 100° C.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with 3 p. c. $KMnO_4$ at 100° C.	5·52 (7·01)	5·77 7·89	6·81 5·16	10·73	11·08
Marcasite with 3 per cent $KMnO_4$ at 100° C. ..	5·25 5·50 (8·67)	7·97	9·42	9·80	7·55

Action of a 5 per cent Potassium Permanganate Solution at 100° C.

This series was decidedly the most satisfactory of the experiments conducted at 100°, and, with the exception of the two-hour oxidations, in case of each mineral shows a remarkably regular increase in the oxidation of the sulphur. It illustrates, too, in the case of the pyrite, the effect of the concentration of the solution due to evaporation. This causes a more rapid rise in the results after three hours' action, and notably between four and five hours. This rise is not so well seen from the table as from the plot of the results given in Pl. xvii. Here this rising of the curve after three hours is very marked as contrasted with the curve of the marcasite oxidations.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 5 per cent Solution of $KMnO_4$ at 100° C.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five hour
Pyrite with 5 p c. $KMnO_4$ at 100° C.	7·95	7·52	9·85	11·86	14·98
Marcasite with 5 per cent $KMnO_4$ at 100° C.. ..	8·38	8·38	13·27	14·85	16·36

(To be continued).

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* Read before the American Philosophical Society, May 18, 1894.—From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

A RE-DETERMINATION OF THE ATOMIC WEIGHT OF YTTRIUM.*

By HARRY C. JONES.

The separation of those elements which occur together in such minerals as gadolinite, samarskite, &c., has always been a matter of considerable difficulty, due largely to the close agreement in the properties of the elements in question. As a consequence of this, what were at one time supposed to be elementary substances have since been shown to be mixtures of two and in some cases of a group of elements, whose compounds were so closely allied in properties as to escape the chemical methods of separation which had been employed.

Spectrum analysis, which has been so fruitful in other fields, has been of value here in showing that the substances which were supposed to be individuals were really mixtures. The atomic weights of these rarer elements have been determined from time to time by analysing their compounds which were thought to be pure, with the result that widely different values have been found for the same element, by different experimenters using different preparations of what was regarded as the same substance. This is well shown in the case of yttrium, whose atomic weight as determined varies from about 105 to 89·1. This is not surprising, since it seems now to be pretty well established that only in one or two cases has even a fairly pure yttrium compound been obtained and used.

This but serves to show that, while the atomic weight of most of the more common elements can be regarded as known to within comparatively narrow limits, the atomic weight of some of the rarer elements may not yet have been correctly determined to within several units.

We need better methods for separating these mixtures, that we may obtain purer compounds from which the atomic weights of the elements can be determined, and any step which will aid us in this direction cannot be without some interest and value.

A method more satisfactory than any hitherto employed for separating yttrium from many of the constituents which occur with it seems to have been found by Prof. Rowland in connection with his study of the spectra of the rarer elements. Although an account of this method has already been published (*Johns Hopkins Univ. Circular*, cxii., 73; reprinted in Chem. News, lxx., 68), yet it is desirable to cite here that part of it which has to do directly with the separation of yttrium by the use of potassium ferrocyanide.

"This is the most useful process, and easily separates the element (yttrium) pure and free from all others. To obtain pure yttrium from the mineral gadolinite, fergusonite, or samarskite: First obtain the crude mixed earths in the usual manner; then separate the cerium group as usual until the absorption bands of neodymium

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* *American Chemical Journal*, vol. xvii., No. 3.

no longer appear. For the complete separation without loss this must be done several times, as much of the yttrium group is carried down with the first precipitate. * * * * *

"The separation of the yttrium from the other elements is effected by precipitating the latter from a weak acid solution by potassium ferrocyanide. For this purpose the filtrate, after separating the cerium group, can be used at once by slightly acidulating with nitric acid, diluting, and adding a weak solution of potassium ferrocyanide. No precipitate should appear at once, but on standing for an hour or so some will come down. Add more potassium ferrocyanide, and repeat until the filtrate no longer shows the bands of so-called erbium. After this it is best to precipitate with oxalic acid or potassium oxalate, and ignite the precipitate so as to get the earth. Dissolve this in nitric acid, and add only water enough to make a very concentrated syrupy solution. Place in a beaker at least 3 inches in diameter, and examine with a spectroscope of low power for absorption bands. Probably the bands of neodymium and "erbium" will appear. Separate the first by sodium sulphate as usual, and the last by potassium ferrocyanide from an acid solution as above. The filtrate will then contain the pure yttrium, whose calcined oxalate will be pure white without trace of yellow. After separation of iron, calcium, and possibly manganese, the earth will be a pure element, as far as I can tell, spectroscopically. However, like Zr, Fe, and many other substances, the addition of Na or K to the electric arc, while obtaining the spectrum, will change the intensity of certain lines of the spectrum, while others are unchanged. If this is considered as evidence of the existence of two elements, then the same evidence will apply to Fe and Zr. The reason for believing that the substance thus found is an element is based on the fact that its spectrum remains unaltered in all minerals, and after all chemical operations, that I have been able to devise. Furthermore, I believe that the new process is not only more easy than any other, but also that it has given a single element for the first time. * * * The yield will, of course, depend on the amount of purity required. From the earths of gadolinite about one-tenth of quite pure yttrium can be obtained and about one-twentieth of very pure.

"I have determined spectroscopically that when, by the above process, the absorption band of "erbium" at last disappears from 3 inches of strong solution, all the other elements have also disappeared.

"By taking the first precipitate several times by potassium ferrocyanide from an acid solution, a mixture of many elements is obtained which contains much of that element to which the so-called "erbium" band is due. By dissolving a weighed quantity of this mixture in nitric acid and water, and examining the band spectrum, I have determined the limit when the band can no longer be seen. Thus I have proved that when the band vanishes from 3 inches of concentrated syrupy solution of yttrium, there cannot exist in it more than ½ per cent of the mixed element as compared with the yttrium, and there is probably less.

"I have not found potassium ferrocyanide useful in the further separation of the elements, but only in separating out α (yttrium) from the others.

"When the neodymium band has disappeared by use of sodium sulphate, all the other elements of the cerium group have disappeared. The element thorium is sometimes present in the crude earths, but disappears after a while from the purified earths. The conditions for its disappearance I have not determined."

A specimen of yttrium oxide, purified by the above-described process, was furnished me by Prof. Rowland for the purpose of determining the atomic weight of yttrium. While the yttria was free from all other rare elements with certainty to within ½ per cent, and probably to within much less, yet the spectrum showed that it might contain traces of calcium, magnesium, iron, and manganese. To remove the traces of these impurities, if present in the yttria, the latter was dissolved in strong nitric acid, and the excess of acid evaporated off on the water-bath. The slightly acid solution was then diluted with a large volume of water, and the yttrium precipitated from the hot solution by ammonia from which all carbonate had been removed, as yttrium hydroxide. The hydroxide precipitated in this manner is somewhat gelatinous, but is more easily filtered and washed than when precipitated from a cold solution. To wash the yttrium hydroxide thoroughly was a somewhat tedious process. The precipitate was allowed to settle, and the supernatant liquid decanted as completely as possible. The precipitate was then treated again with hot water, well shaken, and allowed to settle. The water was again decanted, and the process repeated many times until the precipitate seemed to have been well washed. A small quantity of the hydroxide was then brought on the filter and washed many times with boiling water; this was removed, another small quantity filtered off and washed, and this continued until all of the yttrium hydroxide had been finally washed in this manner. By this process any calcium or magnesium would have been separated from the yttrium.

The yttrium hydroxide was then dissolved in nitric acid and the yttrium precipitated from the acid solution by oxalic acid, which had been repeatedly crystallised from cold water, as yttrium oxalate. The crystalline oxalate was brought on the filter also in small quantities, washed well with hot water, and dried in an air-bath. The dry oxalate was ignited in a platinum crucible over the blast-lamp until the pure oxide remained. In this way any iron or manganese would have been separated from the yttrium.

The yttria thus obtained from the oxalate was pure white when heated over the blast-lamp for a short time. After prolonged heating at a very high temperature it seemed to me to acquire a faint yellow tint. Another observer declared, however, that he was unable to detect a trace of yellow.

The oxide which had been heated for a short time as well as that which had been heated more vigorously, was tested for calcium, magnesium, iron, and manganese by chemical tests, but these failed to show the presence of either of the above-named elements in the yttria.

About 6 grms. of yttria were thus obtained free from all the more common elements and containing as a maximum impurity ½ per cent of the rarer oxides. This is the yttria which was used in the following determinations.

The platinum crucible in which the yttrium oxalate was decomposed to the oxide and which was used throughout the work, was carefully cleaned, and finally, in order to remove any iron which might distil out into the yttria, was heated for a long time in the vapours of ammonium chloride.

All weighings of the platinum crucible, either when empty or when containing the yttrium compound, were made with the crucible placed within a ground-glass stoppered weighing-tube for protection from the atmospheric moisture. This was necessitated by the hygroscopic character of the anhydrous yttrium sulphate. The crucible with its contents was placed in the weighing-tube, while still warm and the tube closed. Further cooling took place in a desiccator over calcium chloride. The stopper was removed from the tube for an instant just before weighing, to insure equalisation of the air pressure. All the weighings were reduced to a vacuum standard. A long-armed Becker balance was used and the accuracy of the weights insured by previous comparisons.

I. *Conversion of the Oxide into the Sulphate.*

The platinum crucible was heated over the blast-lamp to constant weight. The desired amount of yttria, which had been already well ignited, was placed in the crucible and heated again for a short time over the blast-lamp. It was then weighed, re-heated, and re-weighed. In no case was any loss in weight detected, due to the second heating.

The oxide in the platinum crucible was then treated with sulphuric acid of the concentration 1 acid to about 3 of water, and placed in an ordinary air-bath and warmed gently until most of the excess of sulphuric acid had evaporated. The sulphate usually began to crystallise from the solution before all the oxide was dissolved. For this reason large amounts of oxide could not be employed in any single determination, since, with large quantities, one could not be certain that all the oxide had been transformed into sulphate. In one or two of the determinations made there was some doubt on this point, but, that the oxide was completely converted into sulphate in all of the determinations, the results of which are given below, is shown by the fact that the sulphate was found in each case to be entirely soluble in water. The crucible containing the yttrium sulphate, a little free sulphuric acid, and, probably, some acid sulphate, was then placed in an air-bath of such a form that it could be more highly heated than before. This bath consisted of a cylinder of copper about 12 c.m. high and 10 c.m. in diameter, into the opposite sides of which two large holes had been cut and covered with plates of mica. This enabled one to see through the bath at all times. A thick plate of copper was riveted on to the bottom and allowed to project on all sides about an inch beyond the cylinder, to prevent reducing gases from the flame from entering the bath and coming in contact with the yttrium compound. The top of the bath was covered with a plate of iron, and this in turn with a sheet of asbestos. The platinum crucible was supported on a porcelain triangle about an inch from the bottom of the bath. The bath was heated by two triple burners to a little above the boiling-point of sulphuric acid. This removed all free sulphuric acid and decomposed any acid sulphate which might have been present, as was shown by testing a solution of the sulphate in water with methyl-orange, with which acid sulphates give an acid reaction. The sulphate was heated in this bath to constant weight. That there was no decomposition of the sulphate into basic sulphate was indicated by the two facts, that constant weight was quickly established and that the resulting sulphate was entirely soluble in water.

When the anhydrous sulphate was brought in contact with water the greater part of the salt dissolved at once, while a small portion took up water and passed over into the crystalline salt with water of crystallisation. The crystalline sulphate is less soluble than the anhydrous, but on heating the solution every trace of it is dissolved.

A few determinations by this method were lost by accident. In one or two cases, where larger amounts of oxide were employed and not a very great excess of sulphuric acid, the sulphate, when dissolved in water, was found to contain traces of oxide. Below are the results of the ten determinations which were successfully carried to completion:—

	Y_2O_3.	$Y_2(SO_4)_3$.	$3(SO_3)$.	$\left\{ \begin{array}{l} O=16 \\ S=32{\cdot}06 \end{array} \right\}$ At. wt. yttrium.
I.	0·2415	0·4984	0·2569	88·89
II.	0·4112	0·8485	0·4373	88·92
III.	0·2238	0·4617	0·2379	88·97
IV.	0·3334	0·6879	0·3545	88·94
V.	0·3408	0·7033	0·3625	88·90
VI.	0·3418	0·7049	0·3631	89·05
VII.	0·2810	0·5798	0·2988	88·94
VIII.	0·3781	0 7803	0·4022	88·89
IX.	0·4379	0·9032	0·4653	89·02
X.	0·4798	0·9901	0·5103	88 91
Total	3·4693	7·1581	3·6888	
Average				88·94

The mean value of the ten determinations is 88·94, with a maximum value of 89·05 and a minimum value of 88·89. The atomic weight of yttrium, calculated from the total oxide used, 3·4693 grms., and the total sulphate found, 7·1581 grms., is 88·94. All of the above and following calculations are based on oxygen = 16, and sulphur = 32·06; $SO_3 = 80{\cdot}06$.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 22nd, 1895.

Mr. R. T. Glazebrook, M.A., F.R.S., in the Chair.

This meeting was held at the Royal College of Science, South Kensington.

"*On the Objective Reality of Combination Tones.*" By Prof. A. W. Rücker and Mr. E. Edser.

The question as to the objective or subjective nature of combination tones has excited much keen controversy, and the authors have devised some experiments to elucidate this point. These experiments, some of which were exhibited before the Society, show that, under certain conditions, difference and summation tones are produced which are capable of disturbing resonating bodies. As resonator they have, in the first instance, employed a tuning-fork. A piece of thin wood, about 5 inches square, is attached to one of the prongs of a tuning-fork, while a silvered glass mirror is attached to the other, and the pitch is very accurately adjusted to 64 complete vibrations per second. In order to detect any movement due to resonance set up in this fork, the mirror carried by the prong forms part of a system of mirrors for producing Michelson's interference bands. By this means a movement of the prongs of the fork of 1/80,000th of an inch (half a wave-length of light) is shown by the disappearance of the interference bands. As a source of sound a siren was employed, this being one of the instruments which Helmholtz recommends as giving the best results. The pitch of the notes given by the siren was adjusted by noting the disappearance of the beats produced by one of the notes with a bowed fork, or by a stroboscopic method. A large wooden cone, placed between the siren and the resonating fork, served to concentrate the sound on the wooden disc attached to this latter. The sensitiveness of the arrangement is such that when a large Kœnig standard fork, giving 64 vibrations per second, is struck so lightly that an observer with his ear close to the fork cannot detect the fundamental note, the bands instantly disappear. The apparatus, however, is unaffected by any other note, except one of 64 vibrations per second. A number of experiments have been made using various rows of holes on the siren, and in every case when the summation or difference tone corresponded to 64 vibrations per second the interference bands vanished, showing that under the condition of the experiment these tones have an objective existence. An experiment has also been made to determine whether Kœnig's lower beat tone, where the interval is greater than an octave, is objective. In this case, however, the authors entirely failed to get any evidence of such an objective existence. A number of experiments have been made with a view to elucidating the cause of the production of the summation tone, which tend to show that it is not the difference tone of the partials of the fundamental notes. In addition to using a tuning-fork to detect the combination tones, the authors have made use of an instrument which was originally devised by Lord Rayleigh. A light mirror is suspended by means of a fine quartz fibre, and hangs in the neck of a resonator, tuned to the given note, and when at rest is inclined at 45° to the axis of the resonator. Under these circumstances, when the resonator responds, the mirror tends to turn and set itself at right angles to the direction of motion of air in the resonator. The results obtained with this instrument are in complete accord with those obtained by the first method. Up to the present the authors have failed to obtain any evidence of the objective reality of the combination tones produced by organ-pipes and tuning-forks.

The discussion on this paper was postponed till after the reading of the next paper.

"*Some Acoustical Experiments.*" By Dr. C. V. Burton.

(1.) On the Subjective Lowering of Pitch of a Note.

The author has noticed that if a tuning-fork, mounted on a resonator, is strongly bowed, then, if the ear is placed near the opening of the resonator, the pitch of the note heard appears lower than when the fork is bowed very gently or is held at some distance. This subjective lowering of pitch is most marked with forks of low pitch, and, in the case of a fork giving a note of 128 complete vibrations per second, amounts to about a minor third. The author suggests an explanation depending on the supposition that the basilar membrane of the ear behaves as if it consisted of a number of stretched strings of various lengths, each resounding to a given note, and that the appreciation of the pitch of a note depends on the localisation of the part of the basilar membrane which resounds most strongly. Further, he shows that in the case of a stretched string for finite displacements, the string which most strongly resounds to any given note will have a "natural" period longer than the period of the disturbance; the greater the disturbance the longer will be the natural period of the strings most strongly affected. Hence when the intensity of a note increases, the tract of the basilar membrane most strongly affected is displaced in the direction which corresponds to the perception of lower notes.

(2.) Objective Demonstration of Combination Tones.

When two organ-pipes are sounded and alternately separated and brought close together, an observer, at some distance, hears the difference tone much more clearly when the pipes are close together than he does when they are separate. As the position of the pipes with reference to his ear does not appreciably change, the change in the intensity of the combination tone indicates that it has a real objective existence. The author mentioned that he had sounded his two pipes, which give a difference tone of 64 vibrations per second, before the collector of Prof. Rücker and Mr. Edser's apparatus, but without obtaining any motion of the interference bands, and that he was therefore less confident of the correctness of his deductions than he had been before.

Mr. Edser mentioned that Dr. Burton had suggested an explanation of the production of objective tones in the use of the siren which depends on the production of the tones in the wind-chest of the instrument itself, when two rows of holes are simultaneously opened. They had made an experiment which seemed to show that the above explanation was incorrect, for on connecting together the wind-chests of two sirens, fixed on the same spindle, by means of a short length of wide metal tubing, no effect was observed on the bands when the two notes were produced on different instruments having what was practically a common wind-chest.

Prof. Everett (communicated) said he considered the experiments described in the paper proved conclusively the objective existence of the summation tones as distinguished from the supposed beat tones. He had lately been investigating the pitch of the loudest combination tone obtained when two notes having frequencies as 3 to 5 are sounded. Is the frequency of this tone 2, *i.e.*, the first difference tone, or is it 1, which correspondends to the first term of the Fourier series for the periodic disturbance? In the chords 2 to 3, 3 to 4, 4 to 5, &c., the difference of the two integers being unity, the first difference-tone is identical with the first Fourier tone. Where the difference of the two integers which express the chord is not unity, then the writer considers that experiments he has made with strings and pipes show that the first Fourier term is usually the only combination tone that is audible.

Prof. S. P. Thompson considered that care should be taken to define what we mean by the subjective or objective existence of a note, and recommended the use of the term "ear-made tone." There are two very delicate methods which have already been employed for detecting the existence of a given note in the air:—1. The formation of ripples on a soap film stretched over the opening of a resonator tuned to the required pitch (Sedley Taylor). 2. The sounds produced in a telephone connected to a microphone placed on a thin elastic membrane stretched over the neck of the resonator (Lummer). It was very important to limit our acceptance of the demonstration of the objectivity of combination tones given by the authors of the paper to the case actually proved, *i.e.*, to tones produced by the polyphonic siren; it did not necessarily follow that if pure tones produced by tuning-forks were used the same results would be obtained. A number of experiments had been made by Zantedeschi in 1857, in which two notes were sounded, and skilled musicians were asked to record their impression of the third tone present. In 75 per cent of the cases the note recorded was the difference tone. In the remaining 25 per cent it corresponded to Kœnig's beat tone. Kœnig himself had never heard the summation tone in the case of lightly bowed forks. Voigt, in a theoretical paper, has shown that if there are two disturbances, whose mean kinetic energy differ, the Helmholtz tones will be produced; but that if the mean kinetic energy of the two disturbances are equal, the Helmholtz effects soon die out, and you get beat tones or beats. He (Prof. Thompson) considered that Dr. Burton had allowed his perception of tone to be governed by the quality of the note, and that the apparent lowering of pitch was due to the variation in the intensity of the overtones present.

In reply to Prof. Thompson, Dr. Burton said he did not merely perceive a lowering of pitch, but he was able to estimate the change in pitch and say at what instant, as the vibrations of the fork died out, the lowering amounted to a tone or half a tone, &c.

Mr. Boys said he found that by careful attention he could apparently persuade himself that the note in Dr. Burton's experiment was lowered or raised in pitch, or that it remained unaltered. A similar effect in the case of the eye could be obtained with a stereoscopic picture.

The Chairman considered that while Helmholtz's explanation of the production of combination tones might be real, it did not follow that this explanation gave the sole cause of their formation. In particular Helmholtz does not explain why the tones should only be produced by some sources of sound.

Prof. Rücker, in his reply, said he did not deny the existence of Kœnig's beat tones; in fact, he had heard them. They did not lay much stress on the negative result of the experiment they had made to test the objective existence of these beat tones.

UNIVERSITY COLLEGE, LONDON, CHEMICAL AND PHYSICAL SOCIETY.

March 13th, 1895.

"*On the Metallic Alkyl Compounds.*" By N. T. M. Welsmore, M.Sc.

After a cursory general review of these substances, the author went on to describe some unsuccessful attempts of his own to prepare magnesium ethide. The only previous references to this substance were:—Hallwachs and Schafarik, *Annalen*, cix., p. 206 (1859); Cahours, *Ann.*

de Chim. et de Phys., lviii., 3rd series, p. 17 (1860); Wanklyn, *Journ. Chem. Soc.*, xix., p. 129 (1866); and Löhr, *Annalen*, cclxi., p. 79 (1891). The author tried heating ethyl iodide with magnesium filings, at ordinary pressure, in carbon dioxide, and also in hydrogen and in sealed tubes; with magnesium-copper couples, prepared in both the dry and the wet way; and with magnesium-sodium alloy and ethyl acetate. In every case, after the ethyl iodide was used up, a white residue remained, from which, however, no liquid but a trace of higher paraffins could be distilled off. The residue turned brown in air, and deliquesced rapidly, and reacted with water with considerable energy, but, contrary to Löhr's account, gave off no gas whatever. An analysis showed it to be nearly pure MgI_2, almost free from metal if excess of ethyl iodide were used; but containing a little organic matter, possibly paraffins, Mg 8·61, I 90·65, C 0·43, H 0·21 (calculated for MgI_2—Mg 8·63, I 91·37). Magnesium iodide thus prepared was freely soluble in boiling anhydrous ether, from which it crystallisedi with apparently two molecules of ether in large prisms. These were, however, so unstable in moist air that satisfactory combustions could not be made. It was probably this substance which Löhr took to be magnesium ethide. The author could only account for the results obtained by this chemist and other previous observers on the assumption that their magnesium contained zinc or some similar impurity. He had also tried heating magnesium with zinc ethide and with mercury ethide in sealed tubes; but the metal did not appear to be attacked. He concluded with the opinion that the alkyl compounds of beryllium and the compound $N(CH_3)_4I_2$, both claimed to have been prepared by Cahours, could likewise not be accepted without further confirmation. Therefore the rule that only elements situated on the rising portions of Lothar Meyer's curve of atomic volumes are capable of forming ethides is, up to the present, without any sufficiently authenticated exception.

NOTICES OF BOOKS.

Ceylon Manual of Chemical Analyses. A Handbook of Analyses connected with the Industries and Public Health of Ceylon. For Planters, Commercial Men, Agricultural Students, and Members of Local Boards. By M. Cochran, M.A., F.C.S., Professor of Chemistry in the Ceylon Medical College, City Analyst to the Municipality of Colombo, Member of the Ceylon Branch of the Royal Asiatic Society. Colombo: A. M. and J. Ferguson. London: Kegan Paul, Trübner, and Co.; Geo. Street and Co.; J. Haddon and Co. 1895.

This work ought to be highly prized not merely by the classes to whom it more directly appeals, but by every true Briton. Tropical and subtropical agriculture is a pursuit in which a large portion of our national capital is invested, and engaging directly or indirectly a still larger proportion of our industry. It may claim our attention the more urgently as it is now attacked on various sides. The parasitic fungi and animalcules of tropical regions, the synthetic chemistry of Germany, the development of rival products, and the frauds of our own merchants, are all tending to reduce the most valuable lands of India, the West Indies, &c., to useless deserts. Hence the instinct of self-preservation should urge us to bring all the resources of chemical and biological science to bear on the questions involved.

To this good task Mr. Cochran here supplies a valuable contribution. He does not attempt to lay down new or special methods of chemical analysis, but gives us results. He gives us, firstly, a view of the composition of the soils and rocks, showing us the conditions under which such determinations are to be trusted. From the data here supplied it would seem that the soils of Ceylon are very rich in quartz and insoluble silicates. He explains the demands made upon the soil respectively by coffee, tea, cinchona, and cacao, and what manures are needed to keep up a supply of suitable plant-food. Unfortunately, as far at least as coffee is concerned, its failure in Ceylon cannot be remedied by any fertilisers, since it is due to a parasitic fungus. This pest is spreading to Fiji, and we fear to Java. Whether a richer manure would enable the coffee trees to resist the enemy remains to be proved, and perhaps chemical research may lead us to some fungoids able to destroy the scourge.

We next pass to cereals, especially rice. The proportion of phosphoric acid in rice is relatively high. According to the analysis of Kellner, Japanese rice is richer in fatty matter than that of America or of India.

A table is here given showing the average composition of cereal grains as produced in different countries, no Ceylon samples having been apparently analysed. Nor do we find any analyses of Australian or African grains.

As regards the cultivation of rice, the author recommends that it should receive nitrogen both in the form of nitrates and of ammoniacal salts. We regret to find that there is no analysis given of the drainage-waters from rice-fields. This water is said to be especially dangerous, and it would be important to know if this opinion is well-founded, and, if so, whether the mischief is due to chemical ingredients or to the presence of morbific organisms.

The products of the coco nut palm are considered at some length. The yearly value of a coco-nut plantation on good soil is said to be £8 15s. per acre. Attention is called to coco-nut butter, an article recently placed upon the market, and in many respects superior to the margarines.

The tea-crop makes a heavy demand upon the potash, and the phosphoric acid in the soil. There is no special mention of the composition of the soil of the "Mazawattee" estate, which is now, acccording to advertisers, producing such a large proportion of the tea consumed in Britain.

The tannin question is not overlooked. Thr author quotes Mr. Hodge for the statement that the finest teas are those which contain most tannin. A short time ago an attempt was made to depreciate Indian and Ceylonese teas in comparison with those of China, on account of the greater proportion of tannin which the former were asserted to contain. The differences which the patriotic (?) authors so eagerly pointed out seemed due not to any inherent difference in the quality of the tea, but to a different manner of preparation.

Cinchona barks are cultivated in Ceylon on a commercial scale, the principal species being *C. succirubra*, *C. officinalis*, and *C. calisaya*. The proportion of quinine in the *succirubra* natural bark is 1·20 per cent, and in the renewed bark 2·73, in addition to cinchonidine, quinidine, and cinchonine.

The cacao grown in Ceylon is chiefly the Caraccas variety, and it is much esteemed for the manufacture of chocolate. Much of it is exported first to America, and thence to Mexico. According to the analysis of Dr. Tatlock, F.R.S.E., it is exceptionally rich in albumenoids and in the characteristic alkaloid theobromine. It is an exhausting crop as regards phosphoric acid.

Into the useful information on tobacco, areca-nuts, arnatto, coca (erythroxylon), cotton, and datura, space does not allow us to enter.

Pepper, opium, indigo, and ipecacuanha do not seem to rank among the agricultural productions of Ceylon.

The latter part of the book is devoted to sanitary analysis. It is remarkable that the only sample of lemonade which came under the author's hands contained a considerable quantity of arsenic! It is noticed that the sender had "merely tasted it"—a fact which raises some difficult questions.

In fine, to all whom it may concern, this book deserves to be warmly recommended.

Calcareous Cements; their Nature and Uses. With some Observations upon Cement Testing. By Gilbert R. Redgrave, Associate of the Institution of Civil Engineers, &c. Small 8vo., pp. 238. London: C. Griffin and Co. (Ltd.). 1895.

This valuable work has its painful feature in as far as it treats of an industry which was until of late years peculiarly British. It has, however, been lost as far as the export trade is concerned, and it may even be threatened at home. The fact is that the Belgian or German cement manufacturer can employ two men at about the same cost as our English makers can employ one, and can consequently offer his product at a lower price.

Mr. Redgrave points out a further disadvantage to which we are subject, but one more easily remedied. In the method of testing cements we are, he states, seriously deficient as compared with our continental opponents. He gives in full the German rules for testing. He condemns, on the authority of many experiments conducted by German manufacturers and engineers, the various additions to the normal Portland cement materials, as proposed by certain inventors, and hopes that they may be brought within the scope of an amended and extended Adulteration Act—a hope in which we most heartily join. In speaking of the use of sewage-sludge as an ingredient in the manufacture of Portland cement, he seems to us to take too favourable a view of the results. He even ventures on the statement that, in the treatment of sewage, "lime is well known to be the cheapest and best precipitating agent." This assertion, except as regards cost, we must beg leave to contradict most emphatically. This, we have pleasure in adding, is the only questionable statement we can find in a work otherwise calculated to be of great and extended utility.

Agricultural Journal, Published by the Department of Agriculture of the Cape Colony. Vol. viii., No. 3, February 7, 1895.

This issue is exceptionally rich in important matters. We notice a paper by Mr. Otto Henning, C.V.S., on the dissemination of echinococcosis of dogs. The dog is the intermediate host of certain tape-worms, the ova of which are often found in multitudes in his excreta, saliva, and other secretions. Hence it is very important that dogs should have no access to wells, conduits, gathering grounds, and reservoirs subserving municipal or domestic water supplies. The original home of the parasite *Tænia echinococcus*, and consequently of the fearful disease which it occasions, seems to have been Iceland, but it has spread to India and Australia, and is now threatening Africa.

The "Sand Dunes of Gascony" is the title of a very instructive paper, describing the overspreading of valuable agricultural lands, forests, and even villages, by drift-sand from the shore. This was formerly a growing danger in the Landes of Gascony. It has been arrested by measures devised by Brémontier and by Grandjean. The principal agent employed is the so called marrom-grass or sea-matweed, *Ammophila arenaria*, followed up by the maritime pine (*Pinus maritima* of Lamarck).

There is a notice of manuring fields by the process of "Sideration," without any notice of the experiments of M. Ville. The writer, moreover, would prefer to feed cattle with the green crops instead of ploughing them in.

There is a short notice of the alleged impunity of man and other animals against snake-bites if they have once been bitten by a death-snake and have recovered. We suspect recoveries from the effects of the venom of the cobra are very doubtful, unless the part has been immediately amputated.

Alumni Report, Published by the Alumni Association of the Philadelphia School of Chemistry. Vol. xxxi., February, 1895.

A speaker at a Pharmaceutical Meeting pointed out the annoyance occasioned by the practice of colouring beet-sugar with ultramarine. If it comes in contact with an acid, hydrogen sulphide is of course liberated.

Much attention is drawn to the necessity of a cheaper and more convenient supply of alcohol for scientific and technical uses. In this country, on the contrary, we submit without remonstrance to the addition of naphtha to methylated spirits, thus rendering it unfit for all scientific and most technical purposes.

CORRESPONDENCE.

NEW HYDROGEN SULPHIDE GENERATOR.

Monsieur l'Editeur des Chemical News.

Dans votre No. 1843, du 22 Mars, Mr. J. J. D. Hinds décrit et figure ce qu'il croit "A New Hydrogen Sulphide Generator."

Il me sera permis sans doute de faire remarquer que cet appareil, dont je ne discuterai ni les avantages, ni les inconvénients pour l'usage auquel son auteur le destine, n'est qu'une copie exacte de celui que j'ai proposé il y a 15 ans pour la préparation du gaz acide chlorhydrique, décrit et figuré dans la *Zeitschr. f. anal. Chem.*, t. xix., p. 467, et planche 5, figure 7.

Espirant que vous voudrez bien publier les lignes qui précédent dans votre important journal, je vous presente, Monsieur l'Editeur, l'expression de mes sentiments les plus distingués.

L. L. de Koninck.

Liége, le 23 Mars, 1895.

BORON CARBON BATTERY.

To the Editor of the Chemical News.

Sir,—In reply to Mr. Reed's letter of March 15 I beg to inform the writer that there is a vast difference between a platinum element and a platinised one. I admit I use a platinised element, which costs one-fiftieth the price of a platinum one. The writer also states that a primary battery capable of giving 3 volts is by no means remarkable: perhaps he would oblige with a description of a few such cells. As regards a further description of the cell I shall only be too willing to publish this, together with further improvements, when time permits.—I am, &c.,

H. N. Warren.

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

Study of the Iron Chromates.—Charles Lepierre.—The author, when studying the action of the different rays of light upon the chromogenic power of microbia, employed a mixture of ferric chloride and of potassium dichromate as a liquid for absorbing the yellow and orange rays. In the course of some days the sides of the vessel were lined with red crystals, the formation and the composition of which had not been observed and determined. He examined separately the results obtained with ferrous and ferric salts. Concerning the analysis of the products, he states that the elimination of the chrome existing in the solution in the form of alkaline chromate is absolutely useless, since, in the analysis of celestine, a mixture of the salts of strontium and calcium, on the addition of ammonium or potassium chromate, does not give a precipitate of chromate, and the subsequent addition of ammonia and ammonium carbonates precipitates carbonates, and not chromates.—*Bull. Soc. Chim.*, xi.-xii., No. 23.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 10, March 11, 1895.

Argon.—M. Berthelot.—Already inserted.

Losses of Nitrogen caused by Waters of Infiltration.—M. Schlœsing.—The quantities of nitrogen thus carried off are much smaller than we have been led to suppose from the determinations of nitric acid in the drainage waters hitherto published. The losses of nitric acid are distributed very unequally in our fields. Nitrification depends on the organic matter, and is active or slow according to its proportion. Thus the loss of nitrogen is like a graduated tax which falls slightly upon poor soils, and only increases with the richness of the fields.

Analysis of Oyster Shells.—A. Chatin and A. Muntz.—Nitrogen forming part of the organic frame-work of the shells, 0·01 grm.; silica, chiefly in the nacreous layer, 0·07; sulphur, as sulphuric acid, 0·15, besides sulphur in the state of sulphide or in animal compounds, 0·02 grm.; magnesia, 0·4 grm.; manganese, 0·012 grm.; iron, 0·025 grm.; animal matter forming a frame-work in which the mineral substances are deposited; fluorine, about 0·020 grm.; bromine, nearly 0·005 grm.; iodine, 0·003; chlorine, totally absent; carbonic acid, $\frac{45}{100}$ to $\frac{48}{100}$. Phosphoric acid, in common oysters, from 0·03 to 0·04 grm., but in Portuguese oysters (*Gryphea angulata*), 0·075. The proportions of iodine and phosphorus may explain the use of oyster shells in the medical practice of the Middle Ages.

Analysis of Silicon.—M. Vigouroux.—If we allow potassium to act upon a silico-fluoride, there are produced a series of reactions analogous to those indicated by Moissan in the preparation of boron by means of the alkaline metals. A great part of the nascent silicon combines with the potassium in excess, and the iron in which we operate. If we afterwards treat the product of the reaction with water, whilst a further quantity of silicon disappears and is converted into silica in favour of the alkaline metal which has not reacted, the insoluble foreign matters increase the proportion of impurities (silicon, hydrogen, potassium, iron, &c., silicides). In the preparations of amorphous silicon, it seems preferable to use infusible and inert matters, such as silica and magnesia.

Action of Formic Aldehyd upon Ammoniacal Salts.—A. Brochet and R. Cambier.—The authors study the action of ammonia hydrochlorate, both in the cold and in heat. They infer that there exist between ammonia and hexamethyleneamine one or more bases serving as intermediate terms. They are not isolable, but we have been able to demonstrate their existence by the acidimetric study of the solutions, and by fixing these bases in insoluble compounds, such as chloroplatinates or nitroso-derivatives. The other ammoniacal salts give with formaldehyd similar results.

On the Acid Chlorides and Chloro-aldehyds.—Paul Rivals.—A thermochemical paper not susceptible of abstraction.

Splitting Up the Butane-2-oleïc Acid (α-Oxybutyric Acid).—Ph. A. Guye and Ch. Jordan.—The authors have split up this acid into its two components, dextro-rotatory and lævo-rotatory. The separation of these two active isomers is effected very distinctly by the crystallisation of the brucine salt. The crystallisations were effected at temperatures not exceeding 10°, the lowest appearing favourable to the separation.

Daturic Acid.—E. Gérard.—A controversial paper upholding the existence of daturic acid as a chemical individual, $C_{17}H_{34}O_2$, intermediate between the palmitic and the stearic acid, in opposition to J. Dupont, who has recently ("Supplément au Dictionaire de Chimie," by Wurtz) pronounced it a mere mixture of fatty acids. The view of E. Gérard is supported by Noerdlinger and by Wanklyn and Johnstone.

Glycogen in the Blood in Animals in Health or Diabetic.—M. Kaufmann.—The author shows that glycogen is a constituent of normal blood, whilst the blood of animals rendered diabetic by the extirpation of the pancreas contains glycogen in a much more considerable quantity.

Signification of the Liberation of Carbonic Acid by Muscles Isolated from the Body compared with that of the Absorption of Oxygen.—J. Tissot.—There is a complete disagreement between the indications yielded by the quantities of carbonic acid given off and those of oxygen absorbed. The total quantity of carbonic acid disengaged by a muscle isolated from the body cannot be taken as the measure of the physiological activity of this muscle. The absorption of oxygen alone is closely linked to the manifestation of this activity.

Bulletin de la Société Chimique de Paris. Series 3, Vols. xi.-xii., No. 24, 1894.

New Element obtained from Red French Bauxite.—Dr. R. S. Bayer.—Already inserted.

Singular Case of Metallic Precipitation.—J. B. Senderens.—The author (*Soc. Chimique*, May 20, 1894) has observed that metallic lead was deposited upon bars of lead suspended in a neutral solution of lead nitrate at the ordinary temperature. He thinks that the bars of lead may form a galvanic couple, the interior crystals forming one of the elements, and the superficial layers the other.

On a Lead Orthonitrate.—J. B. Senderens.—The orthonitrate has the composition $(NO_4.HPb)_4+H_2O$.

Researches on the Mercuric Sulphates.—Raoult Varet.—A thermochemical paper not adapted for useful abstraction.

Superposition of the Optical Effects of Various Asymmetric Carbons in one and the same Active Molecule.—A. Guye and M. Gautier.—Already inserted.

Active Hydrocarbides with Amylic Radicles.—Miss I. Welt.—The rotatory-power of diamyl is about double that of the foregoing terms. This result is conformable to the ideas developed by Guye and Gautier, according to which the rotatory-power of a substance containing two identical asymmetrical carbons, such as diamyl, must be equal to double the rotatory-power of a diamyl containing an active and an inactive amyl radicle.

Sulphonic Colouring Matters derived from Triphenylmethane.—Maurice Prudhomme.—The sulphonic derivatives of the diamido- and triamidotriphenylcarbinols are colouring-matters known as acid malachite green, acid magenta, alkaline blue, &c. The solutions of these colours, which have a remarkable intensity, are totally decolourised by caustic alkalis. The author concludes that:—1. The alkaline salts of the sulphonic diamido- and triamido-triphenyl carbinols represent, in a state of purity, the colouring-matters known under the general name of acid magentas. 2. The groups $(C_6H_3 . SO_3Na . NR_2)$ in them are electropositive; the OH, connected directly to the methanic carbon, is of an acid nature, capable of exchanging its atom of hydrogen for an atom of sodium in presence of caustic soda or sodium carbonate.

MEETINGS FOR THE WEEK.

Monday, April 1st.—Society of Arts, 8. (Cantor Lectures). "Commercial Fibres," by Dr. D. Morris.
— Society of Chemical Industry, 8. "The German Patent Laws and their relation to Home and Foreign Inventions," by Dr. Carl Pieper.
Tuesday, 2nd.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "My Recent Voyage in Siberia," by Capt. Wiggins.
Wednesday, 3rd.—Society of Arts, 8. "Sand Blast Processes," by John J. Holtzapffel.
— Geological, 8.
Thursday, 4th.—Royal Institution, 3. "Animism, as shown in the Religions of the Lower Races," by E. B. Tylor, F.R.S.
— Institute of Electrical Engineers, 8.
— Mathematical, 8.
Friday, 5th.—Royal Institution, 9. "Argon," by Lord Rayleigh.
— Quekett Club, 8.
— Geologists' Association, 8.
Saturday, 6th.—Royal Institution, 3. "Waves and Vibrations," by Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1845.

A REFORM IN CHEMICAL, PHYSICAL, AND TECHNICAL CALCULATIONS.

By C. J. HANSSEN, C.E.

The study of chemical and physical science, the understanding of the principles involved in chemical and physical phenomena and problems, and the rational application of the results of scientific investigation to practical purposes, would be made easy, if the observations related to these subjects, especially the weight of aëriform substances, were expressed and recorded in a more plain, uniform, and international manner than hitherto. In text-books and publications we find that hardly two authors agree in their statements of specific gravities and specific heats, especially of aëriform substances. Some authors reduce their weights to the 45° latitude and sea-level, others to the latitude and elevation of London, Paris, Berlin, &c. Some prefer the English standard weights and measures and the Fahrenheit thermometer, others the metric weights and measures and the Centigrade thermometer; while some even use both systems in one evening's lecture. In short, a great and serious confusion prevails in these matters, and last, but not least, some of the great masters in the science of heat find wide differences between their calculations and the results of their experiments.

In the following pages the author will endeavour to show that the troubles mentioned can be got over in a very plain way, and to explain a method by which a great many difficult problems may be solved by simple arithmetical calculation, and with greater exactness than by any more elaborate method.

Terms and Units.

The proposed reform and method of calculation requires the use of a system of measure and weight which gives a simple relation between the unit of length (which determines volume), the unit of mass, and the unit of specific gravity. Such a relation is found in the metric system of measure and weight; and this system, therefore, may be used in the proposed method of calculation, and is used here, as no decimal system of measure and weight based on the Anglo-American units as yet is adopted and authorised.*

The *unit of relative gravity* of aëriform substances should be *hydrogen*, because atmospheric air, now commonly adopted as unit, is not a simple substance, but a mixture of at least four different gases, whose proportions are subject to frequent changes, and therefore its gravity is not constant; moreover, its relations to other gaseous substances and to water can only be *approximately* expressed by a long row of decimals, which are tedious to manipulate.

The proper unit of gravity is *hydrogen*, but it is extremely difficult to find the weight of hydrogen accurately by experiment; it is therefore advisable to calculate it from the weight of oxygen and nitrogen, which now have been determined with great accuracy. But even a suitable unit would be useless if its value were not adopted universally. Astronomers of all nations find it advisable and convenient to adopt the meridian which passes through the observatory of Greenwich as the first, and to refer all observations of longitudes to that meridian. In a similar way, physicists and chemists of all nations must adopt a common *circle of latitude*, and all observations and calculations on gravity must be reduced to that latitude. An enormous saving of time and trouble would be the result of this simple measure.

The *weight of oxygen* of 0° C. and atmospheric density, as determined by Regnault, is per cubic metre—

		Kilogrms.
At 45° latitude and sea-level	.. ..	1·42909
In Paris	48° 50′ 11·2″ and 60 metres above sea	1·42913
In London	51° 30′ 49″ ,, 50 ,, ,,	1·42991
In Berlin	52° 30′ 16·7″ ,, 40 ,, ,,	1·43003

The weight of a cubic metre gas decreases from north to south, and at a certain latitude, near the 42°, and 0 metres above sea, it will be 1·4285714285 kilogrms.; or exactly 1/700 of 1000 kilogrms., or of 1 cubic metre of distilled water of 4° C. = 10/7 kilogrm. per 1 cubic metre of oxygen

Nitrogen.—At the Royal Society's meeting, January 31, 1895, it was stated that three samples of chemical nitrogen, prepared from different compounds, had been found to weigh 1·2505 grm. per litre in the mean, but that the heaviest sample was about $\frac{1}{1000}$ heavier than the lightest, and that it was very difficult to free the N entirely of argon. It, therefore, is likely that a litre of *absolutely pure nitrogen* weighs 1·250494 grms.

Assuming this, and taking the atomic weight of N = 14, we get the weight of 1 litre

$$\textit{hydrogen} = \frac{1{\cdot}250494}{14} = 0{\cdot}089321 \text{ grm.}$$

This weight certainly is rather less than hitherto accepted, but 1 volume argon in 4000 volumes of hydrogen would make up the difference, and this minute admixture of A would be difficult to detect and remove.

Oxygen.—The weight of 1 litre of oxygen we find then $0{\cdot}089321 \times 16 = 1{\cdot}429136$ grms., and the weight of 1 litre

Argon $= 0{\cdot}089321 \times 20 = 1{\cdot}78642$ grms.

Multiplying the weights per litre so found by the coefficient 0·999605, to reduce them to weight at the latitude of international gravity, we find at 0° C. and atmospheric pressure the absolute and relative weights. (See Table).

The specific gravity of solid and liquid substances is equal to the absolute weight of 1000 c.c. or 1 litre of the substance, the weight of distilled water at 4° C. being = 1.

Unit of Work.—1 kilogrm. or litre distilled water at 4° C. lifted 1 m. high, = 1 metre-kilogrm.

At the circle of international gravity, where 1 cubic metre oxygen (of atmospheric density at freezing temperature of water, 0° = 273° absolute) weighs 10/7 kilogrms. will be:—

Atmospheric mean pressure = 759·72353 m.m. of mercury. This to be called normal atmosphere; barometric scale to be divided into 1000 parts and pressures denoted: 1·095 atm. N, &c.

1 atm. N = 10·330442 m. column of water = 10330·442 kilogrms. per sq. m. = 8113·5119982 kilogrms. per circular m.

Weight of—		Grms. per litre.	Coeff.		Grms. per litre at international latitude.		
Hydrogen	1	0·089321 ×	0·999605	=	0·08928571 =	5/56 grms.	
Oxygen	16	1·429136 ×	,,	=	1·428571428 =	80/56 = 10·7	grms.
Nitrogen	14	1·250494 ×	,,	=	1·24999994 =	70/56 = 4/5	,,
Carbon	12	1·071852 ×	,,	=	1·07142852 =	60/56 = 15/14	,,
Argon..	20	1·786420 ×	,,	=	1·78571420 =	100/56 = 25/14	,,
Water (liq.) 4° C.	11200				= 1000·0000000	= 1000	

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* See "A System of International Measure and Weight," by C. J. Hanssen (Chemical News, vol. lxiii., p. 215).

Boiling-point of Water 99·975° *C.*—Thermometric scale from freezing to boiling-point divided into 100° normal temperature (100° N).

Unit of Heat.—1 kilogrm. = 1 litre water heated 1° N = 1 *calor.*

Dynamic Equivalent of Heat.— 1 calor = 423·813 m.kilogrms.

Proportion between specific heat of gases at *constant pressure* and constant volume =

$$\gamma = 17 : 12 = 1{\cdot}4166666 : 1{\cdot}000000.$$

Expansion of aeriform substances $\frac{1}{273}$ for every 1° N.

Absolute zero of temperature = −273° N.

For *compound gases and vapours* the calculation of absolute weight, atomic weight, and relative weight is thus:—

Water (vapour) of 273° absolute (0° C.) and atmospheric density H_2O.

2 cbm. hydrogen at 5/56 kgs. = 10/56 kgs. combine with
1 ,, oxygen = 80/56 ,, forming

2 ,, vapour of water = 90/56 ,, ; consequently
1 ,, ,, ,, weighs 45/56 ,, and consists

of $1\frac{1}{2}$ cubic metres of simple gases, and 1 kilogrm. of vapour contains 56/45 cubic metres, and consists of 1/9 kilogrms. of hydrogen and 8/9 kilogrms. of oxygen; or of 56/5 × 1/9 = 56/45 cubic metres of hydrogen, and 7/10 × 8/9 = 56/90, or 28/45 cubic metres of oxygen of 273° absolute and atmospheric density.

The *relative weight* of the vapour (hydrogen being = 1) is found by the proportion—

5/56 kgr. (H) : 45/56 kgr. (vapour) = 1 (H) : 9 (vapour).

Ratio of Chemical Contraction.—In combining to form vapour the 3 cbm. of simple gases have contracted into 2 cbm.; consequently, the ratio of contraction is 3 : 2.

The *atomic weight* of the compound is found by the proportion—

Original volume of simple gases : ultimate volume of compound = relative weight : atomic weight = 3 : 2 = 9 : 6.

Composition of Liquid Water.—By weight, as shown above, hydrogen is 1/9 and oxygen 8/9 of the weight of vapour, and, consequently, also of liquid water. 1 cubic metre of liquid water of 4° C. (273° absolute) weighing 1000 kilogrms. consequently consists of—

Kgs.	Kgs.	Kgs.		Cbm.	
1000/9 =	$111\frac{1}{9}$ =	111·111111	or	11200/9 = $1244\frac{4}{9}$	hydrogen.
8000/9 =	$888\frac{8}{9}$ =	888·888888	or	5600/9 = $622\frac{2}{9}$	oxygen.
	1000 water =	1 cbm. consists of		$1866\frac{2}{3}$	cbm. of

simple gases, and the *relative weight* of liquid water, as compared to hydrogen, is found by the proportion—

1000 kilogrms. (water) : 5/56 kilogrms. (hydrogen) = 5600 : 5 = 11200.

The *atomic weight* of liquid water is found by the proportion—

$$\left.\begin{matrix}\text{Volume of}\\ \text{simple gases}\\ \text{in 1 cbm. of}\\ \text{compound}\end{matrix}\right\} : 1\text{cbm. hydrogen} = \left\{\begin{matrix}\text{relative}\\ \text{weight of}\\ \text{com-}\\ \text{pounnd}\end{matrix}\right\} : \left\{\begin{matrix}\text{atomic}\\ \text{weight}\end{matrix}\right.$$

$$1866\tfrac{2}{3}\text{ cbm.} : 1\text{ cbm.} = 11200 : 6$$

The *volume of steam* of atmospheric density and 0° C. (273° absolute) would—if steam of atmospheric density could exist as *steam* at that temperature—be found thus—

1 cubic metre water consists of $1866\frac{2}{3}$ cubic metres of simple gases of atmospheric density and 0° C. (273° absolute). In combining, these contract at the ratio 3 : 2, and consequently form 2/3 × $1866\frac{2}{3}$ = $1244\frac{4}{9}$ cubic metres vapour, of the initial temperature and pressure of the component gases,

At the boiling temperature of water, 100° C. = 373° absolute, the $1244\frac{4}{9}$ cubic metres of steam would expand to

$$\frac{1244\frac{4}{9} \times 373^\circ\,\text{N}}{273^\circ\,\text{N abs.}} = 1700{\cdot}2849 \text{ cubic metres}$$

saturated steam of atmospheric pressure of 1 cubic metre water; or exactly—

$$\frac{1755}{2984} \text{ cubic metres}$$

steam of that temperature and pressure, consequently are formed of 1 kilogrm. water and 1 cubic metre of such steam weighs exactly

$$\frac{2984}{1755} \text{ kilogrms.}$$

From the foregoing it follows that steam of any given pressure and temperature always is nine times the weight of an equal volume of hydrogen of equal pressure and temperature.

Atmospheric Air.—The discovery of *argon* calls for a revision of the composition of air. At international latitude, atmospheric density, and 0° N, I calculate—

1 cubic metre air (purged of CO_2) weighs 1·2925977 kilogrms., and contains—

				Grms.		Grms.
208880	c.c.	O at 1/700	=	$298\frac{2240}{5600}$	=	298·4000
781231	,,	N at 1/800	=	$976\frac{3017}{5600}$	=	976·5388
9889	,,	Argon at 1/560	=	$17\frac{3690}{5600}$	=	17·6589
1000000	,,	= 1 cbm. air	=	$1292\frac{3347}{5600}$	=	1·2925977 kilogrms.

and 1 kilogrm. air (purged of CO_2) contains—

161597·08768	c.c.	O	at 1/700 grm.	=	230·85300	grm.
604388·42592	,,	N	,, 1/800 ,,	=	755·48550	,,
7650·48640	,,	A	,, 1/560 ,,	=	13·66150	,,
773636·00000	c.c. air (purged of CO_2)			=	1000·00000 = 1·0000	grm. kgr.

1 grm. = 773·636 c.c. air.

The N and A are mixed in the proportion 79/80 N + 1/80 A (by volume).

3, Valdemarsgade, Copenhagen, V.,
March 4, 1825.

(To be continued).

A WAX FOUND IN THE TREATMENT OF COTTON AND LINEN FIBRE FOR THE MANUFACTURE OF PAPER.

By CLAYTON BEADLE.

It is occasionally observed that the iron walls of a beater in which cotton and linen pulp is disintegrated becomes coated with a film, which protects the iron against the action of the bleach, &c. It appears that this film is not formed under ordinary conditions of treatment, as its occurrence is not generally known to paper-makers. This wax-like film, when of sufficient thickness, can be readily scraped from the sides of the beater. A case of this formation was brought before my notice about two years ago. The formation of this film was so rapid as to cause inconvenience, and to necessitate constant scraping of the sides of the beaters, lest portions should detach themselves and form yellow spots in the pulp.

I examined samples of this substance taken at different times, and found that it consisted of alumina, iron, and lime salts, mixed with a substance soluble in ether. The latter substance has a sweetish smell and generally resembles bees'-wax. It has a saponification equivalent (p.c.) of 19·46 (KOH), and a very definite melting-point of 47·5° C. The wax on saponification gave 91·04 per cent insoluble fat acids. Samples were taken and examined at different times, and were found of constant composition. The raw material that gave rise to the formation of this substance had been previously treated under pressure in a 3½ per cent solution of NaOH, and afterwards thoroughly bleached in calcium hypochlorite solution at 32° C. The wax doess not make its appearance until the bleached material is disintegrated. At the back of the beater-roll a thin film may sometimes be seen on the surface of the water. This in time builds itself up on the sides of the beater. The characteristic sweetish odour of the isolated wax can be traced back often to the bleached material, which sometimes smells strongly.

I think there is evidence that this substance does does not exist in the raw fibre, but is formed in the cell wall during treatment. It is hardly probable that this substance, which is readily dissolved by soda, should survive the treatment with alkali under pressure. The odour which is characteristic of this substance is not noticed in the raw material until after the warm bleaching, and appears to be more developed after the bleached material is allowed to lie heaped up in a dense condition for some time. By altering the mode of bleaching of the raw materials, the occurrence of this waxy substance can be prevented. I found in one batch of cotton fibre, that smelt strongly of the waxy substance, that the alcoholic extract amounted to 2·87 per cent, and, when treated with ether afterwards, the ethereal extract amounted to 0·73 per cent.

The separation of the wax in the beater is merely a mechanical one, and is probably due to the fact that it intimately penetrates in the fibre. The knives of the beater-roll, which tear the ultimate fibre asunder, release the wax, which floats on the surface as a fine film, and quickly builds itself up on the metallic surface with which it comes in contact. I succeeded in at one time collecting about 50 lbs. of the deposit, which was found, on extraction with ether, to contain 77·54 per cent of wax.

4, New Court, Lincoln's Inn.

NITRO-CELLULOSE FILTERS.

By H. N. WARREN, Research Analyst.

The above-named filters have been prepared and used by the author to great advantage during the examination of phosphates and other like precipitates, which always present more or less difficulty as regards incineration when in contact with carbonaceous substances. They are best prepared by the following means:—Chemically pure filter-papers that have been extracted with hydrofluoric acid, after having been thoroughly dried, are introduced, one at a time, into a mixture of equal parts by volume of nitric acid, 1·5 sp. gr., and good commercial oil of vitriol; each paper is allowed to remain for five minutes, and they are afterwards placed upon a sheet of glass, and washed with a full water supply until free from every trace of acid, the papers being afterwards carefully dried. They should be preserved in stoppered bottles, as they are slightly hygroscopic. By this means a paper is prepared corresponding to the formulæ of a trinitro-cellulose, burning almost instantaneously, and perfectly free from residue; these retain perfectly the finest precipitates, and at the same time filter much faster than ordinary papers. A paper possessed of slower combustion, and corresponding to dinitro-cellulose, may be obtained by using the ordinary nitric acid in admixture with twice its volume of vitriol; these, however, must not be brought in contact with ethereal solution, since dinitro-cellulose is readily soluble in that menstruum. A quicker and at the same time less expensive method may be employed, by using a mixture of one volume of ordinary nitric acid with two of vitriol, together with a small quantity of hydrofluoric acid; into this mixture the ordinary cut filter circles may be introduced similar to the previous cases, the hydrofluoric acid at the same time removing the silica; papers thus treated showing a diameter of 5 inches, the ash of which amounted to 0·003 grm., showed after incineration a weight approximating to only 0·0025 grm.

The papers in either case, when containing precipitates, burn without any explosive violence, and are perfectly safe as regards projecting any substances they may contain.

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A NEW FLASK.

By HARRY M. SMITH.

In the estimation of sugar by means of Pavy's solution it is very desirable to have a white background to the flask in which the titration is conducted. It occurred to me that the lower part of the flask might be made of white and opalescent glass. These flasks, as made for me by Mr. Müller, of 148, High Holborn, are about 2½ inches in diameter, and the lower third is almost porcelain-like in appearance. They give very satisfactory results, aud, although specially designed for use in sugar analysis, they would, I think, be found useful in other processes where colour changes are concerned.

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SYNTHETIC EXPERIMENTS IN THE PYRAZOL SERIES.*

Part I.

By R. von ROTHENBURG.

(Continued from p. 153).

On Alkylised Pyrazolons.

(3)-Methylpyrazolon.—This substance was obtained at first from hydrazin and acetacetic ester, but afterwards from acetic anilide. The author has since obtained it by the action of hydrazinhydrate upon dehydracetic acid, tetrolic acid, β-isonitrosobutyric acid, or their esters and methyloxyazolon. In all cases the composition and the melting-point were correct.

(3)-Methyl-(4)-allylpyrazolon.—The allyl-group, on account of its non-saturated nature, might possibly have reacted with hydrazin hydrate and disturb the formation of pyrazolon. This conjecture proved to be unfounded. The compound forms leaflets melting at 195°. It is sparingly soluble in water, but abundantly in organic solvents, especially in heat. Its composition is $C_7H_{10}N_2O$.

(3)-Methyl-(4)-trimethylen-*o*-pyrazolon is formed from molecular quantities of hydrazin hydrate and acetyl-trimethylencarbonic ester. It crystallises from dilute alcohol in leaflets fusible at 197°. It is readily soluble in all solvents; it affords the characteristic reaction with ferric chloride, but does not react with diazo-salts or nitrous acid. Its composition is $C_6H_8N_2O$.

(3)-Phenylpyrazolon.—First obtained by Thun, at the instigation of Curtius, by condensing benzoyl acetester with hydrazin hydrate. It is fusible at 236°. The author has obtained a number of its derivatives.

Among the pyrazolons with condensed nuclei, the

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* From the *Journal Praktische Chemie*.

author describes (3, 4)-benzoisopyrazolon, discovered anhydride of ortho-hydrazinbenzoïc acid, which may be regarded as the quinoline of the pyrazolone series.

A condensation of pyrazolon itself with benzene is not conceivable, such as has become known in (4, 5)-benzopyridazolon. But the author has obtained the naphthaline of the pyrazolon series, *i.e.*

(3, 4)-Pyrazolono-pyrazolon.—If an excess of hydrazin hydrate is added to an alcoholic solution of (4)-isonitroso-pyrazolon-(3)-carbonic acid it turns green and deposits a greenish grey precipitate, sparingly soluble in all solvents; it separates from dilute acids in white, granular crystals which are decomposed at 125—126°. The substance gives the characteristic reactions of pyrazolon. Its composition is $C_4H_2N_4O_2$.

It was not found practicable to arrive at (3)-bispyrazolon.

Hexahydrobenzo-(3, 4)-dipyrazolon was obtained by boiling an alcoholic solution of 1 mol. succinyl-succinic ester with hydrazin hydrate and acetate (2 mols.). It becomes an intense yellow with a blue fluorescence, and on cooling deposits a yellow granular powder. It is sparingly soluble in all solvents, and separates from hot dilute sulphuric acid in yellowish green and light brown prisms and needles fusible at 256—257°. It is a true pyrazolon derivative, coloured reddish yellow by nitrous acid and deep chestnut-brown with ferric chloride. Its composition is $C_8H_8N_4O_2$.

Hexahydrobenzodipyrazolone in an alkaline solution forms with the diazobenzene-salts a blood-red azo-compound.

Hexahydrobenzo-(4)-benzal-(3, 4)-dipyrazolon is formed by heating pyrazolon with its equivalent of benzaldehyd to 120—130°. It is practically insoluble in all solvents, and forms a reddish yellow granular powder quite unaffected by a temperature of 280°.

Hexahydrobenzo-(1, 1)-dimethyl-(3, 4)-dipyrazolon is formed by heating pyrazolon for some hours to 100° in a sealed tube with methyliodide and methyl-alcohol. Very sparingly soluble, yellowish, fusible above 250°. Reacts with nitrous acid with a red colouration.

Dihydrobenzo-(1, 1, 2, 2)-tetramethyl-(3, 4)-di-isopyrazolon is obtained from the foregoing on prolonged heating in a tube to 160—180° with a large excess of methyliodide and methylic alcohol, and can be freed from the accompanying impurities by its insolubility in alkalis and ammonia. More easily soluble than the foregoing. Does not react with nitrous acid and forms granular crystals fusible above 250°.

Hexahydrobenzo-(1, 1)-diacetyl-(3, 4)-dipyrazolon is formed on heating for a short time pyrazolon with 2 mols. acetic anhydride; a colourless granular powder fusible above 250°. It is soluble in alkalis. Its silver salt is sensitive to light, and it reacts with nitrous acid.

Dihydrobenzo-(1, 1, 2, 2)-tetracetyl-(3, 4)-di-isopyrazolon.—Is formed on submitting the former to a prolonged heat with an excess of acetic anhydride, and may be purified by its insolubility in alkalis and ammonia. It does not react with nitrous acid, and forms no silver salt. It is the most stable of its group, and crystallises from acetic ether or alcohol in globular aggregations, or white nodules, fusible above 250°.

The Constitution of the Pyrazolons. Isomerism and Tautomerism of the Pyrazolons. Course of the Reaction, and Conditions of the Formation of the Pyrazolons.

The somewhat considerable new material unfortunately does not admit of any remarkably enlarged insight into constitution of the pyrazolon ring. It must further be admitted that the constitutional determinations of Knorr have proved absolutely correct as against the objections of Nef.

So much is certain that pyrazolons and isopyrazolons are tautomerous and isomeric only in their isomers; that is, no isomers are capable of existence, the isomerism of which is occasioned solely by the position of the double bond in the nucleus. It must, however, be remarked that there is a second tautomerous form still more unstable than isopyrazolon, in the state of an (3)-oxypyrazol, and that its existence may be regarded as demonstrated, and that the following three configurations exist:—

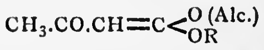
I. Isopyrazolon. II. Isopyrazolon. III. (5)-Oxypyrazol.

A fourth conceivable form seems excluded on account of the entirely uniform behaviour of the derivatives of hydrazin hydrate and phenylhydrazin.

Only the form I. is capable of existence in the free state, II. in an acid, and III. in an alkaline solution, in which the pyrazolons behave exactly like phenols, *e.g.*, in the formation of azocompounds—a reaction which leaves nothing to be desired in point of complete analogy. In like manner, I am of opinion that the alkaline salts of acetaceticester contain the metal combined with oxygen, although I agree with Brühl and Von Pechmann in ascribing the ketone formula to the β-ketone esters. Whether we ascribe to the alkali-compounds the formula—

$$CH_3COAlc{:}C.HCO_2R,$$

or—



$$CH_3.CO.CH{=}C{<}^{O\,(Alc.)}_{OR}$$

is quite non-essential for the formation of the azo-compounds, but I prefer the latter formula on account of its perfect analogy with the pyrazolons.

On the basis of the previous expositions, I must take up a sceptical attitude concerning the alleged discovery of isopyrazolon.

Such substances are capable of forming pyrazolons which contain a carboxyl-group (or a group equivalent in its stage of oxidation, *e.g.*, anilide, ester, &c.), and, in addition, in the β-position an aldehydic or ketonic-group, or a group which may re-generate an aldehydic or ketonic group or act as such (β-isonitrosopropionic acid = β-aldoximacetic acid) or in which the α and β atoms of carbon are connected by combination of acetylene (propiolic acids).

On Pyrazolidon.

As the three-fold non-saturated propiolic acid forms with hydrazin hydrate pyrazolon it might be expected that acrylic acid would yield pyrazolidon. The reaction agreed with the theory. Hydrazin hydrate reacts spontaneously with acrylic acid with an energetic liberation of heat. If heated it reacts with hydrazin acetate or tartrate. The solution, if it has an acid reaction, is neutralised with soda, shaken out with ether, and dried with calcium chloride.

On fractionation, the base boils at 133—135°, has a pungent odour like that of pyrazolon, mixes perfectly with ether, alcohol, &c., dissolves slightly in water, not in alkalis, easily soluble in acids; the specific gravity is smaller than that of water. Its composition is $C_3H_6N_2O$.

A characteristic of pyrazolidon is its behaviour with oxidising agents, which readily convert it into pyrazolidon, or the derivatives of the latter. It is purely a base: it does not dissolve in alkalis or in ammonia. It forms no silver salt, but at once reduces an ammoniacal solution of silver.

Pyrazolidon and Ferric Chloride.

Ferric chloride, if added in small proportion, colours the solution of pyrazolidon a violet red. The colour disappears on heating. On the addition of more ferric chloride, there appears the characteristic violet-brown colouration of the pyrazolons.

If pyrazolidon is treated at a boiling heat with the calculated quantity of a standardised solution of ferric chloride the solution becomes nearly colourless. The oxidation takes place almost quantitatively, if the iron is precipitated with alkali, and if paradiazotoluol sulphate is added with customary precaution.

Pyrazolon-(4)-*p*-azotoluol is precipitated in small red crystals, fusible at 219°.

It was not practicable to form an azo-compound of pyrazolidon, the result being merely a deep brownish red oil of an intense odour.

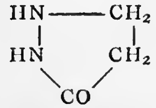
Pyrazolidon and Nitrous Acid.

Nitrous acid (as also bromine, mercuric oxide, silver oxide, lead peroxide, and similar agents) oxidise pyrazolidone to pyrazolon.

The original greenish colour depends, doubtless, on a true nitrosamine of pyrazolidon. We introduce nitrous acid until the solution takes a deep orange-yellow colour, neutralise cautiously with ammonia, and precipitate with silver nitrate pyrazolon-(4)-isonitroso-silver, which is then purified by re-solution in ammonia and cautious precipitation with acetic acid.

The Constitution of the Pyrazolidons. Isomerism and Tautomerism, Course of the Reaction and Conditions of the Formation of Pyrazolidon.

The pyrazolidons, as dihydropyrazolon, can only have the following constitution:—



The isomers can differ only in respect of the substituents, and phenomena of tautomerism do not occur; especially no hydroxyl-group can be formed, since these compounds are insoluble in alkalis and ammonia, form in alkaline solutions no azo-compounds, and are of a purely basic character.

As to the course of the reaction in the formation of pyrazolidon, it is not yet decided whether it is an additive process or the substitution process of a β oxy-carbonic acid formed intermediately.

The conditions of the formation of pyrazolidon are the presence of a carboxyl (or equivalent) group and fixation of ethylene between α- and β-carbon atoms, or β-hydroxyl in the nascent state.

(To be continued.)

ON THE

PREPARATION OF AMORPHOUS SILICON.

By M. VIGOUROUX.

The method generally taken for the preparation of amorphous silicon is that of Berzelius—reduction of the double silicon and potassium fluoride (fluosilicate) by potassium. The analysis proves that the silicon of Berzelius is far from pure.

H. Moissan having obtained pure amorphous boron by the reduction of boric acid in excess, by means of magnesium, we endeavoured to prepare amorphous silicon in the same manner, by heating silica with magnesium. Silicic acid being less readily fusible than boric acid, this preparation, which had been previously tried by several experimentalists, presented some difficulties.

In 1864 Phipson mentions the reductive action of magnesium upon silica. In 1867 Farkinson (? Parkinson) mentions the presence of magnesium silicide and silicate among the products of the reduction.

Gattermann (*Berichte*, xxii., p. 186) showed anew with what ease magnesium reduced silica, whether natural or artificial. On heating over a Bunsen burner he obtained a mass which, in hydrochloric acid, gave off a gas spontaneously inflammable, if the magnesium is in excess, and, with the halogens formed silicon chloride, bromide, and iodide, if the silica is in excess.

Lastly, Winckler (*Berichte*, xxiii., p. 2642) endeavoured to prepare silicide of the formula Mg_2Si. He caused magnesium to act, firstly, upon silicon, and then upon silica. He pulverised two atoms of the metal with one of the oxide, and on heating only 0·20 grm. of this metal in a glass tube he experienced a violent explosion, the tube being shattered and the contents projected. If he operated in a current of hydrogen, the tube was not broken when he used 5 grms. or upwards of the mixture. There was formed a heterogeneous product, marked with blue and brown. On heating a mol. of silica with one of silicon, he did not obtain silicon protoxide. He infers that this latter compound does not exist.

We have sought for the conditions most favourable for the production of amorphous silicon, and, even when operating upon large quantitites, we were able to conclude—1st. That to avoid any explosion it is merely necessary to employ absolutely dry materials. 2nd. That if the mixture is very intimate the product is homogeneous.

Three series of experiments have been performed:—(*a.*) The proportion of magnesium was exactly necessary for the production of the silica with the formation of magnesia. After treatment there was obtained a powder of a chocolate colour in which were found silicides and numerous brilliant grains of silicon melted by the heat evolved at the moment of reduction; it is therefore requisite to moderate the reaction, (*b.*) We employed a variable excess of silica. There is formed less melted silicon, little or no magnesium silicide; but the treatments were very tedious and the yield always very slight. (*c.*) We operated in presence of magnesia. If we dilute the two active ingredients with this inert matter, the rise of temperature was much less. If we varied the proportions of magnesia, we were finally able to avoid the formation of melted silicon and that of magnesium silicide. We may then apply this result to the preparation of amorphous silicon.

To this end we take the proportions of magnesium and silica indicated by the formula—

$$SiO_2 + 2Mg = Si + 2MgO,$$

to which was added a quantity of magnesia equal to a fourth of their weight.

We used:—Silica, 180 grms.; magnesium, 144 grms.; magnesia, 81 grms. The silica selected was ground quartz met with in this state in trade. The magnesium was the powder employed for photographic purposes. The magnesia is the ordinary product, ignited strongly before the experiment. These three substances, mixed so as to form a very homogeneous powder, are poured into an earthen crucible holding double their bulk, covered with a layer of magnesia, and then dried as perfectly as possible.

When we wish to effect the reduction we introduce the crucible, still hot, into a Perrot furnace, previously heated to redness. In two or three minutes the reaction is set up. It is manifested by crackling, which lasted for some moments, and a bright incandescence of the entire mass; sometimes a little magnesium distilled and escaped between the crucible and the cover. In a minute afterwards the fire is extinguished, and the crucible withdrawn but kept closed. It is found that the material has increased in bulk, which shows the necessity of large crucibles.

The reaction takes place at 540°, measured by the thermo-electric forceps. This indication may be utilised whenever it is required to dry the product; it is sufficient to introduce the crucible when charged into the Perrot furnace kept at 300 or 400°. We may thus remedy the inconvenience of large crucibles, which do not easily find room in medium furnaces. It is sufficient to substitute for them smaller ones, each covered with a second crucible inverted and pierced at the base, which may project through the opening in the cover of the furnace. Thus most of the charges have been made in crucibles No. 14, fitted with a No. 12 crucible as a lid. It is necessary that the whole should be raised to the temperature of reduction. It may be produced by placing the mixture on a plate and covering it with magnesium powder. It is sufficient to apply a lighted match; the metal burns, and the heat evolved by the latter primes the reaction, which then continues spontaneously.

When cold it is a mass quite homogeneous, of a light maroon colour, without brown or blue marblings, porous and brittle, and easily detached The inside of the crucibles has become a greyish blue, which shows that magnesium has exerted upon it a reductive action. If we wish to avoid this inconvenience the interior of the crucibles must be lined with magnesia, or the portions which have been in contact with the sides are rejected.

The powder is at first treated with hydrochloric acid. If the mixture was sufficiently intimate there is not a trace of hydrogen silicide, showing that no magnesium silicide has been formed. Boiling sulphuric acid removes the last traces of magnesium free or combined. Then, by two or three alternate treatments with hydrofluoric acid in the water-bath and with boiling sulphuric acid, the silica and the silicides can be removed. The process is completed with ebullition in hydrochloric acid, and then in water.

After desiccation we obtain a powder of a maroon colour, perfectly homogeneous.

If chemically pure materials are employed, we obtain a silicon containing 99·09 to 99·69 per cent; with commercial products the figures are not very different.—*Comptes Rendus*, cxx., p. 94.

THE CHEMOMETER.*

By W. OSTWALD.

(Continued from p. 154).

On the basis of Faraday's law it is now possible to conduct the processes between electrolytes so that they cannot take place without a simultaneous movement of electricity, and that the quantities of work which may be obtained from the chemical process may be manifested in the form of electrical energy. As, on the one hand, the electrical energy is equal to the chemical, and, on the other, the factors of capacity on either hand, the quantities of matter, and the quantities of electricity are proportional according to Faraday's law, the magnitudes of intensity, the chemical potential, and the electromotive force are proportionally to each other, and the electrometer serves as a chemometer in the sense above expounded. And as electromotive forces can be distinguished only by number and sign, we have a universal measure of the chemical potential, or, as we may justly name this magnitude, of the chemical affinity.

In order to illustrate the result of an example, we may take any single chemical reaction, *e.g.*, the precipitation of silver nitrate by sodium chloride. In order to utilise this process electro-chemically we must resolve it into two parts, which certainly occur simultaneously but separate in space, as we otherwise could not transform the chemical energy into electrical, but should obtain it as heat. We obtain this if we take two silver plates, placing the one in the solution of silver nitrate, and the other in that of sodium chloride. If both solutions are connected by an indifferent electrolyte, the two silver plates show a very distinct difference of potential of rather more than 0·3 volt; and if we set up the current by means of a conductive connection of both plates, silver chloride is formed on the plate immersed in sodium chloride, whilst metallic silver is deposited on the other plate. The total quantity of metallic silver remains therefore unchanged; a certain quantity of silver nitrate has disappeared; on the other hand, an equivalent quantity of silver chloride is formed: finally, the NO_3 ions of the silver nitrate and the Na ions of the sodium chloride have travelled into the intermediate vessel and have formed sodium nitrate. The chemical result of the total process is exactly the same as if sodium chloride is directly added to the solution of silver nitrate.

In a similar manner all chemical processes between electrolytes may be transformed into voltaic chains, care being only taken that the chemical process cannot take place without the electrical. Thus much trouble has been taken concerning the chain formed by one of the most important processes—the neutralisation of an acid by a base. Such a one is obtained if we plunge, both into the acid and the alkali, a plate of platinum or palladium saturated with hydrogen. On suitable connection there is then, on the side of the alkali, an absorption of hydrogen, whilst on the side of the acid there ensues an equal liberation of hydrogen. At the same time the current between the solutions, the basic kathions, and the acid anions, are moved towards each other in corresponding numbers, and thus neutralised. The electromotive force of neutralisation is about ¾ volt for powerful acids and bases, and for weaker ones is of course smaller.

It would take us too far if I were to explain only all the typical cases of the possible reactions between acids, bases, and salts. The remark must suffice that it is always practicable, and that for each such reaction we obtain the accompanying electromotive power.

A further remark must be made. The electromotive power of the circuits described is essentially composed of two items, the potential differences which exist at each electrode in respect to the liquid. We do not therefore require a direct measurement of all combinations, but may be content with determining all the combinations with one electrode, in order if we have, *e.g.*, twenty different substances, to calculate the electromotive forces of all the two hundred combinations which are possible between them all.

Thus the problem of the chemometer is solved for electrolytes.

Considering the importance of the result and the general character of the duction employed, it may be useful to show the accuracy of the result in another manner. To this end I will make use of a form of the second main theorem of energetics, which, although it has been used in principle by Lord Kelvin years ago, has only been lately expressed in general terms. The theorem is—Whatever is in equilibrium in any manner must be in equilibrium in every manner, and its proof lies in the truth that whenever it is not fulfilled it is possible to construct a *perpetuum mobile* of the second kind, a combination in which quiescent energy sets itself spontaneously in motion, which according to experience is impossible.

If we now suppose two substances in chemical equilibrium, which we arrange in a suitable manner, but showing an electrical difference or an electromotive power; then let the current be set up and any machine be driven by its means, until an electrical equilibrium is produced in consequence of the chemical changes accompanying the current; the existing chemical equilibrium must then be disturbed, but we can restore it by the interaction of the substances. The conditions are then given for obtaining electric work anew, and so on. The same series of inferences holds good if we begin with the assumption that the substances are in electrical but not chemical equilibrium.

Chemical and electrical equilibrium must therefore be simultaneously present. If the former is wanting, the latter cannot exist. Both deviations must take place in such a manner that the chemical processes depending on the electromotive force are engaged in an approximation to equilibrium.

(To be continued).

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* From the *Zeitschrift fur Physikalische Chemie.*

IS ARGON CONTAINED IN VEGETABLE OR ANIMAL SUBSTANCES? *

By GEORGE MACDONALD, B.Sc., and
ALEX. M. KELLAS, B.Sc.

At Professor Ramsay's suggestion, experiments were undertaken to see whether argon could be obtained from nitrogenous vegetables or from animal tissues.

Method :—A few grms. of the substance, after drying if necessary, were ground to a fine powder, desiccated at 110° C., until the weight was constant, and a nitrogen estimation performed by Dumas's method. It was supposed that any argon compound would be decomposed, when the argon would come off along with the nitrogen. The gas was collected in a nitrometer over well-boiled concentrated potash solution, whence it was transferred to a small gasholder containing water which had been boiled for some hours. The gasholder was connected with an apparatus similar in general arrangement to that used by Prof. Ramsay in July last, which enabled the gas to be dried and purified from hydrocarbons, carbon monoxide, or hydrogen, the nitrogen being absorbed by being passed and re-passed over magnesium turnings kept at a temperature of about 600° C. A three-way stopcock enabled the magnesium tube and the purifying and drying tubes adjoining it to be connected either with the second gasholder or with a "Sprengel," so that any residual gas could be pumped off, and the tubes exhausted before admitting the gas. The gas pumped off was collected in a piece of hard glass tubing; it was then mixed with oxygen prepared by heating potassium permanganate, and sparked down until no further diminution of volume occurred, when excess of oxygen was known to be present. The remaining gas was transferred by a gas pipette to a tube standing over mercury, and the oxygen present absorbed by potassium pyrogallate solution. Only one experiment was carried through to the end in each case as the results seemed conclusive, although several determinations of nitrogen were made.

Peas were selected as a typical vegetable, and the following is a summary of the results :—

Expt.	Weight of Desiccated Peas taken.	Volume of Nitrogen collected (corrected for temp. and press).	Weight of Nitrogen.	Percentage of Nitrogen in Dried Peas.
	Grms.	C.c.	Grm.	
1	8·9446	465·8	0·5843	6·53
2	8·9455	466·8	0·5856	6·55
3				

342 c.c. of the volume collected in the first experiment (which was done in two parts) was passed over the heated magnesium until so much nitrogen was absorbed that both gasholders were full of water, and the residue was then left for about twelve minutes in the tubes, the magnesium being kept heated so that absorption of nitrogen might continue. On connecting with the pump a pressure of about 2 inches was registered, and the volume of gas pumped off had a volume of nearly 8 c.c. After sparking down with excess of oxygen, 6·8 c.c. of gas was left, and on absorbing by a strong solution of potassium pyrogallate (stronger than Hempel recommends for complete absorption) 0·12 c.c. of gas remained, which is less than 0·04 per cent of the volume taken. To see if this bubble of gas consisted of carbon monoxide, two experiments were performed with the oxygen used: 9 c.c. gave 0·2 c.c. residue, and 11·2 c.c. gave 0·25 c.c. residue, with about the same strength of pyrogallate.

As the quantity of oxygen used in sparking down was over 20 c.c., it might safely be concluded that there is no appreciable quantity of argon in peas (or at least that the argon cannot be obtained with the nitrogen by Dumas' method).

The experiment with regard to the presence of argon in animal tissues was also negative in its results. Mice were selected for the experiment, because the nitrogen from the whole animal could be conveniently collected by Dumas' method. The crucial experiment was carried out in the same way as before.

From three mice 550 c.c. of nitrogen was obtained. This was absorbed by heated magnesium as usual, but the residual gas was left for over an hour in the tubes after the gasholders had been emptied, so that on connecting up with the pump only a few m.m. of pressure was registered, and the total gas pumped off occupied about 1 c.c. After sparking down with large excess of oxygen about 10 c.c. remained, which gave a residue of 0·2 c.c. with alkaline pyrogallate, which would be about 0·36 per cent of the volume taken.

Very careful experiments were undertaken to determine the exact percentage of nitrogen contained in mice, as the volume from the first experiments seemed too high. Two experiments with complete mice gave the following results :—

	Weight of Mouse.	Percentage of Water lost at 110° C.	Percentage of Nitrogen in Desiccated Animal.
	Grms.		
A	13·7	73·1	11·0
B	12·5	70·5	10·6

A Kjeldhal determination of the nitrogen in a small quantity of mouse A, by Mr. Frye, gave 9·6 per cent, so that the high percentage seems confirmed.

A POSSIBLE EXPLANATION OF THE TWO-FOLD SPECTRA OF OXYGEN AND NITROGEN.*

By E. C. C. BALY, A.I.C.,
1851 Exhibition Scholar in University College, London.

The two spectra of oxygen are shown to be of a different nature. They behave differently, and reasons are given for their being in all probability the spectra of different gases. They may either be two spectra produced by different vibrations of the oxygen molecule, or they may be the spectra of two different modifications of oxygen, or the spectra of two distinct gases resulting from a dissociation of oxygen, a combination of which is called oxygen.

It appeared worth while to undertake experiments with a view of testing the last of these. Oxygen was sparked in an apparatus similar to that used by Prof. J. J. Thomson in his experiments on the electrolysis of steam. Hollow platinum electrodes were used, each one of which was connected with a Sprengel mercury pump. In the first experiments the distance between the electrodes was 35 m.m, and the highest pressure compatible with the appearance of the two spectra was made the starting-point of the experiments. In these first experiments it was 380 m.m. The density of the oxygen before sparking was determined, and taken as a test of its purity. The fractions obtained from the anode and cathode were weighed, and the results are given. They follow the lines of J. J. Thomson's results, inasmuch as with long sparks a lighter fraction was obtained at the cathode, and with short sparks a heavier fraction. The fractions from the anode were not so definite as from the cathode, though the difference was in the right direction. The probable maximum error of weighing was 0·0001 grm. This meant exactly one in the second decimal place of the density obtained. The general accuracy of the results may be gauged from the densities of unsparked oxygen obtained.

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* A Paper read before the Royal Society.

* Abstract of a Paper read before the Roal Society.

Density of Cathode Fraction with Long Sparks.	Density of Oxygen Unsparked.	Density of Cathode Fraction with Short Sparks.
15·78	15·88	16·00
15·79	15·87	16·01
15·80	15·89	16·02
15·79	15·88	16·04
	15·88	16·06
		16·05

Mean of results of other observers = 15·887.

Density of cathode fraction from oxygen, previously for three days fractionated with short sparks, 15·75.

The experiments are still in progress.

A RE-DETERMINATION OF THE ATOMIC WEIGHT OF YTTRIUM.*

By HARRY C. JONES.

(Concluded from p. 157).

II. *Conversion of the Sulphate into Oxide.*

Yttrium sulphate was prepared by dissolving the oxide in dilute sulphuric acid and evaporating the solution to a small volume on the water-bath, when the sulphate crystallised out. The mother-liquor was then poured off, and the sulphate dried by pressing between filter-paper. The desired amount of the sulphate was placed in the platinum crucible, which had been heated over the blast-lamp to constant weight, and itself dried to constant weight in the cylindrical air-bath previously described, at a temperature a little above the boiling-point of sulphuric acid. The weighed sulphate was then decomposed to the oxide in the platinum crucible over the blast-lamp. During the latter part of the heating the lid was removed from the crucible, and the oxide heated in direct contact with the air.

The heating was continued until the oxide had attained a constant weight, and the oxide was tested in every case for the presence of sulphate. When constant weight was reached under the conditions employed, every trace of sulphate had been decomposed to oxide.

To test the reliability of this method a weighed amount of yttrium oxide was converted into sulphate by the method first described, and then this sulphate decomposed to oxide by the method just described. If the method of decomposition of the sulphate was trustworthy, then the same amount of yttrium oxide should have resulted from the decomposition of the sulphate as was originally used. Two such tests were made, and in both cases the amount of oxide obtained from the sulphate agreed with the amount originally used to within a tenth of a m.grm.

Below are the results of the ten determinations by this method, which were finished satisfactorily. Here also an occasional determination was lost by accident.

	$Y_2(SO_4)_3$.	Y_2O_3.	$3(SO_3)$.	$\left\{ \begin{matrix} O = 16 \\ S = 32·06 \end{matrix} \right\}$ At. wt. yttrium.
I.	0·5906	0·2862	0·3044	88·91
II.	0·4918	0·2383	0·2535	88·89
III.	0·5579	0·2705	0·2874	89·03
IV.	0·6430	0·3117	0·3313	88·99
V.	0 6953	0·3369	0·3584	88·89
VI.	1·4192	0·6880	0·7312	88·99
VII.	0·8307	0·4027	0·4280	88·99
VIII.	0·7980	0 3869	0·4111	89·02
IX.	0·8538	0·4139	0·4399	88·99
X.	1·1890	0·5763	0 6127	88·96
Total	8·0693	3·9114	4·1579	
Average	.. .. ..	.. .. ..	.. ..	88·97

The mean atomic weight from the ten determinations is 88·97, the highest value found being 89·03, the lowest 88·89. The atomic weight of yttrium calculated from the total sulphate, 8·0693 grms., and the total oxide, 3·9114 grms., is 88·97.

The agreement between the two series of determinations is satisfactory, and the atomic weight of yttrium, as determined from the oxide which I employed, is about 88·95.

Historical Sketch.

To show how widely the results of the different determinations of the atomic weight of yttrium which have been made differ from one another, I give the following brief sketch:—

The earliest determination was made by Berzelius (*Schweigg. J.*, xxii., 336; xvi., 422; *Pogg. Ann.*, viii., 186) in 1818. From his analysis of the carbonate. Ostwald ("Lehrbuch zweite Auflage," Bd. i., 122) has calculated the atomic weight Y = 105. Meyer and Seubert ("Atomgewichte der Elemente"), from Berzelius's analysis of the sulphate, have calculated the atomic weight Y = 96·77. (O = 16.)

From the analysis of the sulphate made by Popp, 1864 (*Liebig, Ann. Chem.*, cxxxi., 191), Ostwald has calculated the atomic weight Y = 102·13. From Popp's determination of yttrium in the sulphate, by precipitation as oxalate and weighing as oxide, Meyer and Seubert have found the atomic weight Y = 101·90. (O = 16)

From the determinations of water in the sulphate, made by Delafontaine, 1865 (*Liebig, Ann. Chem.*, cxxxiv., 109), Meyer and Seubert have found the atomic weight Y = 97·86. (O = 16.) From his determinations of yttrium in the sulphate they calculate Y = 96·64. (O = 16.)

Bahr and Bunsen, 1866 (*Liebig, Ann. Chem.*, cxxxvii., 21), dissolved yttrium oxide in sulphuric acid, evaporated on the water-bath, and gradually heated above the boiling-point of sulphuric acid. From the results Meyer and Seubert give Y = 92·80. (O = 16.) Pure oxide was transformed into basic nitrate, and in this way was found Y = 92·48.

The above determinations are now only of historic interest, since, in the light of more recent discoveries, it is almost certain that in each case mixtures of yttrium wsth other rare earths, some of which were known and others not suspected, were employed.

Clève and Höglund, 1873 (*Bihang. till. Vet. Aks. Handl.*, 1873, i.. iii., No, 8), seem to have had the purest material up to their time. By converting the oxide into the sulphate they found Y = 89·58. (O = 16, S = 32·06).

Clève, 1883 (*Bull. Soc. Chim.*, xxxix., 120) converted as pure yttria as could be obtained into the nitrate, and repeatedly fractioned by means of oxalic acid. Finally he obtained a small quantity of yttria whose molecular weight remained constant. This was separated by means of oxalic acid into four fractions, each of which gave a sulphate containing about the same quantity of yttria. 23·2091 grms. of the sulphate gave 11·2568 grms. of the oxide. From this follows Y = 89·1. (O = 16, S = 32·06.)

There seems to be no doubt that Clève's yttria was the purest hitherto employed, and his determination has, up to the present, been justly regarded as nearest to the true atomic weight of the element.

The value which I have found is about 0·15 of a unit lower than that of Clève, which argues for a corresponding increase in purity in my material over that of Clève's, since the impurities commonly present have a higher atomic weight than yttrium. The impurity in the oxide which I used, which from spectrum analysis cannot exceed ½ per cent, and is probably less according to Rowland, is very likely a remnant of the "erbium" group which was not completely separated by the potassium ferrocyanide. The true atomic weight of the element yttrium is then, in all probability, a little lower than 88·95, the value found from the yttria which I employed.

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* *American Chemical Journal*, vol. xvii., No. 3.

Crookes (Chem. News, lxx., 81) has recently raised the question as to whether the atomic weight of the yttrium obtained by Rowland had been determined. The work described in this paper, which was carried out before Crookes's communication was seen, will, it is hoped, answer that question satisfactorily.

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.†

By AMOS PEASLEE BROWN.

(Continued from p. 155).

I. *Table Showing Average Relative Oxidation of Sulphur in Pyrite and Marcasite by Solutions of* $KMnO_4$ *at* 22° *and at* 100°. (See Pl. xvii.).

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.	On Pl.
Pyrite $\frac{1}{100}$ N. cold	·78	1·17	1·38	1·74	1·72	22° P_1
Marcasite $\frac{1}{100}$ N. cold	1·07	1·86	2·04	(1·25)	2·38	22° M_1
Pyrite 1 per cent cold	1·71	(1·43)	1·86	1·85	1·80	22° P_2
Marcasite 1 per cent cold	1·22	1·21	2·06*	2·32*	2·24	22° M_2
Pyrite 3 per cent cold	2·55	2·27	2·80*	2·55	2·55	22° P_3
Marcasite 3 per cent cold	2·80	2·25	2·87*	2·88*	2·80	22° M_3
Pyrite 5 per cent cold	2·77	3·09	2·77	2·89	3·02	22° P_4
Marcasite 5 per cent cold	2·31	3·41	3·30*	3·16	3·78	22° M_4
Pyrite $\frac{1}{100}$ N. 100°	4·05	4·72	3·36	2·04	5·64	100° P_1
Marcasite $\frac{1}{100}$ N. 100°	3·17	3·84	3·76	5·63	5·61	100° M_1
Pyrite 1 per cent 100°	6·03	6·98	8·38	6·11	6·88	100° P_2
Marcasite 1 per cent 100°	6·43	5·93	8·56	7·40	9·10	100° M_2
Pyrite 3 per cent 100°	6·26	6·83	6·81*	10·73	11·08	100° P_3
Marcasite 3 per cent 100°	6·47	7·97	9·42	9·80	(7·55)	100° M_3
Pyrite 5 per cent 100°	7·95	7·52	9·85	11·86	14·98	100° P_4
Marcasite 5 per cent 100°	8·38	8·38	13·27	14·85	16·36	100° M_4

* Obtained by omitting discordant results.

II. *Table Showing Selected Results of the Oxidation of Sulphur in Pyrite and Marcasite by Solutions of* $KMnO_4$ *at* 22°. (See Pl. xviii.).

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.	On Pl.
Pyrite $\frac{1}{100}$ N. cold	·78	1·17	1·38	1·74	(1·72)	22° P_1
Marcasite $\frac{1}{100}$ N. cold	1·07	1·86	2·04	(1·25)	2·38	22° M_1
Pyrite 1 per cent cold	(1·71)	1·47	1·85	1·90	1·89	22° P_2
Marcasite 1 per cent cold	1·16	1·29	1·93	1·95	2·15	22° M_2
Pyrite 3 per cent cold	(1·65)	2·31	2·80	(2·62)	2·81	22° P_3
Marcasite 3 per cent cold	(2·72)	2·33	2·87	2·88	2·83	22° M_3
Pyrite 5 per cent cold	2·39	3·03	3·22	(2·89)	3·24	22° P_4
Marcasite 5 per cent cold	2·52	3·06	3·82	(3·16)	4·17	22° M_4

No very marked difference in the rate of oxidation is brought out by this series of experiments, the amount of sulphur oxidised never having reached the critical point in pyrite, as shown by Prof. Smith's oxidations with the current already described. This point at which the rate of oxidation of sulphur in pyrite suffers a change was found by Prof. Smith to be between 21 and 22 per cent from the results of a very large series of current oxidations.* The explanation for this being the critical point in the oxidation of pyrite will be given in the discussion of its constitution. The experiments with permanganate oxidation simply show then that up to near this point (the highest point reached in the pyrite oxidation was nearly 15 per cent) the relative rates of oxidation of the two minerals do not differ widely from each other, but that marcasite oxidises somewhat faster than pyrite. This is simply what has long been known and recognised in regard to atmospheric weathering.

As will be seen when the constitution of these minerals is considered, marcasite cannot have a critical point in regard to oxidation of its sulphur.

The experiments thus far described had for their object the removal of sulphur. On the other hand, a number of ways of attacking the iron were tried and with more interesting results. In these trials reagents were selected which would attack the iron more energetically than the sulphur. Among these may be classed the experiments of solubility in acids.

Hydrochloric acid (hot or cold, concentrated or dilute) has little action on these minerals. Pyrite was treated for one hour with boiling concentrated HCl, of specific gravity 1·20 in covered beakers, and showed in the solution only 2·56 per cent of iron out of 46·67 per cent. Marcasite, treated in the same way, gave an identical result. Similar experiments at the ordinary temperature were tried with both minerals, by digesting for three days with excess of concentrated hydrochloric acid and with excess of $2HCl+3H_2O$, but even after three days the action was very slight in both cases. Pyrite gave with both concentrated and dilute acid the same result—a solution of 1·51 per cent of iron. Marcasite gave almost identical results. The concentrated hydrochloric acid solution showed 1·51 per cent of iron, the dilute solution 1·89 per cent. No evolution of hydrogen sulphide was detected by lead paper in either case. Concentrated sulphuric acid at boiling temperature decomposes both minerals, with evolution of sulphur dioxide and the separation of sulphur, but the action is very slow and seems to take place more readily with pyrite than with marcasite. Pyrite digested with concentrated sulphuric acid at boiling temperature for one hour showed 14·81 per cent of the iron dissolved, but marcasite under like conditions was only attacked in one hour to the extent of 12·77 per cent of iron. Trials were also made in the cold, but did not differ materially from the results obtained with HCl.

More important results were obtained by conducting dried hydrochloric acid gas over the minerals at an elevated temperature. In these trials 0·2 grm. of the mineral was placed in a porcelain boat and heated in a glass tube in a strong stream of the gas. The sulphur in the series of experiments at the lower temperature was collected by passing the gas through bulbs containing Br+HCl; at the higher temperatures, the residue in the boat was analysed and the sulphur lost estimated by difference. In the experiments at low temperature the entire tube was exposed to a temperature of 210°, as determined by thermometer. The HCl was passed over in a strong stream for one hour. The action at this temperature was slight; the results obtained do not, however, show the entire amount of sulphur removed, as some remained in the cool end of the tube, from the dis-

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† Read before the American Philosophical Society, May 18, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

* Private communication from Prof. E. F. Smith, 1893.

sociation of the hydrogen sulphide. As the action was so slight, no attempt was made to collect and estimate this sulphur remaining in the tube. In the bromine and hydrochloric acid solution was found sulphur as follows:—

Pyrite at 210° in current of HCl (*a*)	0·94
,, ,, ,, ,, (*b*)	0·93
Marcasite at 210° in current of HCl (*a*)	0·77
,, ,, ,, ,, (*b*)	0·59

More marked results were obtained by increasing the temperature. Similarly conducted experiments were carried out at 310° and 325°, the time of heating ranging from one to three and one-half hours. The temperature of 310° was graded by keeping it between the melting points of $NaHSO_4.H_2O$ (300°) and $NaNO_3$ (313°), the higher temperature was between the last 313° and the melting point of $KClO_3$ (334°). After the HCl had been passed for a sufficient length of time, the tube was allowed to cool (with the gas current continued until cold) and then the remaining sulphur estimated by oxidising the contents of the boat with nitric acid and potassium chlorate and precipitating and weighing as $BaSO_4$. The amount found, subtracted from 53·33 per cent, gave the loss of sulphur. In this case the results obtained by oxidation were reversed, the pyrite lost more sulphur than the marcasite. This is an expression of the fact that the hydrochloric acid gas (or its contained Cl) acts more vigorously on the iron of pyrite than on that of marcasite. The results of the reaction were in each case ferrous chloride in the boat and free sulphur in the tube, the latter from dissociation of the hydrogen sulphide. No ferric chloride was seen in the tube, except a trace with the pyrite. Each mineral was heated for one hour at 310° in a current of the gas and showed loss of sulphur as follows:—

Pyrite heated at 310° for one hour in HCl, sulphur lost	10·73
Marcasite heated at 310° for one hour in HCl, sulphur lost	7·19

About the same relative amounts were lost on heating for three and one-half hours at 325°. The results thus obtained were as follows:—

Pyrite heated at 325° for three and one-half hours in HCl, sulphur lost	17·13
Marcasite heated at 325° for three and one-half hours in HCl, sulphur lost	10·70

Besides these two experiments, pyrite was heated for one hour at a red heat in a stream of the gas. A copious sublimate of ferrous chloride was found in the tube, with a trace of ferric chloride and sulphur. This time the loss was 46·47 per cent of sulphur. It seems evident from these experiments that, as above stated, the iron in pyrite is in a condition that is more readily acted on by hydrochloric acid than is the iron in marcasite. It will be proved that the iron in marcasite is all ferrous, while part of that in pyrite is ferric, and this is probably the explanation of the above phenomenon. All of the iron in each case described above would form ferrous chloride ($FeCl_2$) on account of the reducing action of the hydrogen sulphide formed. Under the conditions of the above experiments, the critical point developed in the oxidation of pyrite was not reached, but it is not likely that it exists with this reagent, or if there be a critical point it is not 21 per cent. The thought suggested itself to me that perhaps some sulphur would be lost in pyrite if it were heated to 325° in a neutral atmosphere, and that this might account for the difference shown in the loss of sulphur in the two minerals. This proved not to be the case. Pyrite heated in this way in an atmosphere of nitrogen gave no appreciable loss after one hour at a temperature of 325°.

Instead of hydrochloric acid gas, the action was tried of ammonium chloride at temperatures up to 335° and in an atmosphere of nitrogen. Under these conditions the sulphur was combined as ammonium sulphide probably and did not exert such a reducing action on the iron. These experiments were conducted as follows:—0·2 grm. of the finely pulverised mineral was mixed with 0·5 grm. dry ammonium chloride and introduced (in a porcelain boat) into a glass tube. Test samples of $NaHSO_4.H_2O$ and $KClO_3$ in sealed tubes were used to regulate the temperature. All air was displaced in the tube by nitrogen and a slow current of nitrogen passed through the tube before heating. Under these conditions with marcasite, sulphur ammonium sulphide were found sublimed in the tube along with ammonium chloride, and in the boat there was found much ferrous chloride without any ferric chloride, but in the case of the pyrite there was formed a large proportion of ferric chloride, which sublimed on the tube towards the end of the operation. The heating was conducted slowly in each case and continued until all ammonium chloride was sublimed from the boat, the temperature of 335° not being exceeded during this time. The entire operation lasted about twenty-five minutes in each case. Three trials of each mineral were made and with the same result in each case; with marcasite only ferrous chloride was found in the boat and no iron in the tube, pyrite always gave much ferric chloride and little ferrous. The amounts of sulphur removed are probably not very significant; they showed the following results:—

Pyrite heated with NH_4Cl lost sulphur (*a*) ..	7·02
,, ,, ,, ,, (*b*) ..	7·10
Marcasite ,, ,, ,, (*a*) ..	9·50

(To be continued).

CORRESPONDENCE.

THIO-ACETIC ACID.

To the Editor of the Chemical News.

Sir,—Being interested in the discovery by Messrs. Schiff and Tarugi of the use of ammonium thio-acetate as a substitute for sulphuretted hydrogen, which was described in your columns a few weeks back, I made a quantity of that reagent according to their directions, and noticed the following peculiarities not mentioned in the paper by the authors:—

That the precipitate of cadmium sulphide, obtained by the use of this reagent, instead of being yellow, is of a reddish colour, and might easily be mistaken for antimony.

Stannic salts produced a brown-black precipitate of stannous sulphide, instead of the usual yellow stannic sulphide.

And, lastly, having left about 100 c.c. in a tight-stoppered flask, on returning to it after a few days I found the flask had been burst, presumably by the accumulation of gas generated from the reagent.

The thio-acetic acid was made as usual by distilling glacial acetic acid with phosphorus pentasulphide, and it was dissolved in ammonia without being purified by re-distillation.

I should like to know if anyone else has noticed these peculiarities, and also if anyone could explain the cause of the one last mentioned.—I am, &c.,

Fredk. Soddy.

The Laboratory,
University College, Aberystwyth.

Appointment.—Dr. A. W. Crossley, Ph.D. (Würzburg), M.Sc. (Victoria), Berkeley Fellow and Demonstrator of Organic Chemistry in the Owens College, Manchester, has been elected Demonstrator of Chemistry in the Medical School of St. Thomas's Hospital in succession to Dr. W. H. Ince, who has been appointed Government Chemist at Trinidad.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 11, March 18, 1895.

Attempts to Cause Argon to Enter into Chemical Combination.—M. Berthelot.—Already inserted.

Nomination.—The Academy proceeded to the nomination of a free member, *vice* the late F. de Lesseps. M. Carnot was elected, having obtained an absolute majority of votes.

Transformations of Fibrine of the Prolonged Action of Weak Saline Solutions.—A. Dastre.—The solution upon which the author was experimenting contained a fibro-globuline α, analogous to fibrinogene, coagulable at 55°; a fibro-globuline β, coagulating above 75°; certain peptones or proteoses giving the reactions of the proteoses of gastric digestion, and traces of peptones. With chlorides and iodides the action is as energetic in weak as in strong solutions. With fluorides at 5 per cent the reaction is minimal or null.

Action of Nitrous Oxide on Metals and Metallic Oxides.—Paul Sabatier and J. B. Senderens.—The oxidising action of N_2O upon metals and their oxides is very imperfectly known. It is known that potassium and sodium if slightly heated in this gas burn vividly, and that iron, manganese, zinc, and tin, if heated to redness, are oxidised more or less quickly. The gas, carefully purified and dried, was passed over the substances in question at temperatures always below 500°. Cadmium heated to near the melting-point, 320°, is gradually oxidised and volatilised, forming a brown deposit of oxide on the sides of the tube. Lead, obtained in a state of fine division on reducing litharge by hydrogen, is slowly oxidised about 300°, and reproduces yellow litharge. Iron, reduced at redness in a prolonged current of hydrogen, burns below 170°, forming red ferric oxide. Reduced cobalt burns incompletely about 230°, being re-converted into brown cobaltous oxide (cobalt 82·1 per cent). Nickel, reduced, is oxidised with incandescence at 300°, forming monoxide. Reduced copper remains unchanged at 200°, but above 250° it is slowly transformed into red cuprous oxide. Near dull redness we may obtain a slight incandescence. *Lower Oxides.*—Greenish yellow manganous oxide, obtained by reducing the sesquioxide, is oxidised with incandescence about 350°, and forms light brown Mn_3O_4. Tungsten bioxide, WO_2, of a blackish brown colour, is transformed without incandescence at 450° to the blue oxide, WO_2, not mixed with tungstic anhydride. Molybdenum sesquioxide, Mo_2O_3, is slowly changed into the violet oxide, MoO_2. Brown stannous oxide, SnO, burns at 400°, forming white stannic oxide, SnO_2. Purple cuprous oxide, Cu_2O, prepared previously, is not oxidised at 350° in nitrous oxide; its weight remaining identical. Black vanadium sesquioxide, prepared by reducing with hydrogen vanadic anhydride, Va_2O_5, is not modified below 500°. Yellow uranium oxide reduced in hydrogen at bright redness, forms uranous oxide, of a maroon brown, which is not altered by nitrous oxide at 450°. If the reduction is effected at a lower temperature the uranous oxide is black and burns in nitrous oxide at about 400°, forming black oxide, U_2O_5.

The Combination-Heats of Mercury with the Elements.—Raoul Varet.—A thermo-chemical paper not adapted for useful abstraction.

Isomeric States of Mercury Oxides.—Raoul Varet.—Like the iodides, the mercury oxides assume a red and a yellow state; both stable in the cold, and thus differing from the iodides. The conversion of the yellow mercury oxide into the red state gives rise to no appreciable thermic effect. This explains why the red and the yellow varieties are equally stable at ordinary temperatures. As to the two iodides, the transformation of the yellow into the red state is accompanied with a liberation of heat of +3 cal. The more exothermic compound only is stable in the cold.

Formation-Heat of some Compounds of Iron.—H. Le Chatelier.

On the Chloroaldehyds.—Paul Rivals.

Crystalline Isomer of Monochloroaldehyd.—Paul Rivals.—These three thermo-chemical papers do not admit of ready abstraction, and cannot claim insertion in full.

Mercuric Compound of Thiophene permitting its Separation and Determination in Commercial Benzenes.—G. Deniges.—The author has endeavoured to isolate thiophene in the form of an insoluble compound, and the presence of sulphur in its mol. led him to employ for this purpose the salts of mercury, the affinity of which for organic sulphur compounds is well known. The author proposes to develop his procedure in a future paper.

The Amorphous State of Melted Bodies. — C. Tanret.—The author studies the state of substances originally crystalline, but rendered amorphous by fusion.

Derivatives of Active α-Oxybutyric Acid. (1. Butanoloïc Acid).—Ph. A. Guye and Ch. Jordan.—The authors have split up racemic oxybutyric acid into its two optical isomers, and have undertaken the study of its principal active ethers.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 1, 1895.

Rotatory Power of some Ethers of β-Methyladipic Acid.—P. Freundler.—Methyladipic acid crystallises in white tablets fusible at 91—92°. It distils unaltered at 211° (at a pressure of 15 m.m.). Its specific rotatory power at 2 per cent in an aqueous solution is $(\alpha)_D = +8{\cdot}4°$. The author remarks that the methyladipic ethers differ from the tetra-substituted tartaric ethers by the absence of acid radicles.

Reactions occasioned by the Decomposition of Sodium Thiosulphate in Fixing Photographic Images.—M. Seyewitz and G. Chicandard.—On employing alum and thiosulphate in the proportion of twenty times more thiosulphate than alum, we require, to avoid all decomposition, a weight of commercial sodium bisulphate equal to about the fifth of the weight of the alum. In a mixture of 15 grms. thiosulphate and 60 of alum, we do not require more than the hundredth part of the weight of the alum.

On the Emetics.—E. Maumené.—The author calls in question the formula of tartaric anhydride, or, as he calls it, tetrafilic acid. This formula, he contends, should be written $C_8\,{}_2H_2O_8\,{}_{20}$. In a memoir on the hydrocarbides, he has maintained that the ratio $C_8 = 48$ to H_2, or 24 to 1, cannot be true. The exact proportion is 123/5, and not 120 to 5. From an examination of the emetics of silver, sodium, rubidium, potassium (ordinary tartar emetic), and lead, M. Maumené concludes that in an acid, a salt, or any other compound, water can never play a double part (water of combination, water of crystallisation); it is united in a single mass to the anhydrous substance in the general law. An anhydride is that from which we may separate a maximum of water without causing it to lose its essential character. The remark of Berzelius of a constant ratio between the oxygen of the anhydride and that of the bases is not by any means strictly accurate. The composition of all bodies, without exceptions, is subject to the general law of the actions of mixture, sometimes to that of actions of contact, and to no other. The replacements of bodies by others, called substitutions, present always the relations of which we speak, the two terms of which vary exclusively according to the weight of the bodies in action. Isomers, the number of which is greater or smaller in compounds of any nature, vary according to the molecular condensation and the union of the condensed substances with others in the relations of the general law.

New Process for obtaining Dicarbonic Acid (Mellic Acid).—E. Maumené.—The neutral potassium tetrafilate, *i.e.*, tartrate, resists heat up to 280°. At this temperature it becomes coloured if not entirely pure, and loses all the water which it still contains, yielding pure neutral dicarbonate, water, and a little carbon oxide. The salt, very soluble in water, easily yields the acid on transformation into a lead salt and treatment with hydrogen sulphide.

Method of Formation of α-Phenylquinoleine.—Amé Pictet and H. Barbier.—The condensation of formanilide with acetophenone recalls to a certain extent the formation of acridine by the dehydration of formyldiphenylamine, and seems to prove the existence in the pyridic nucleus of quinoleine of a bond between the nitrogen and the carbon γ.

Phenotripyridine.—A. Pictet and H. Barbier.—Phenotripyridine crystallises from alcohol in small prismatic needles, almost colourless. It melts at 236°, and distils unchanged at a much higher temperature. It is insoluble in water, moderately soluble in absolute alcohol and ether, and very soluble in benzene and chloroform. Its character as a tertiary base is shown by the fact that it yields neither an acetylic nor a nitrosic derivative. The authors describe the dehydrochlorate, monohydrochlorate, nitrate, sulphate, and chromate.

Volumetric Determination of Nitric Acid.—D. Monnier and H. Auriol.—By means of an apparatus which cannot be described without the accompanying plate, the authors compare the quantity of hydrogen evolved by causing one and the same quantity of sodium amalgam to react upon pure water, and again upon the aqueous nitric acid in question. The difference of the two volumes corresponds to the hydrogen consumed by the reduction of the nitrates.—*Archiv. Sc. Phys. et Nats. de Genève.*

Adherence of Aluminium and of other Metals to Glass.—Ch. Margot.—Aluminium, magnesium, cadmium, and zinc, to the exclusion of other metals, have the property of leaving upon glass, and in general upon all substances having bases of silica, metallic traces which are not removed by vigorous friction—washing.—*Archiv. Sc. Phys. et Nats. de Genève.*

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on April 1, Sir James Crichton-Browne presiding. The following were elected Members:—Mr. Lockett Agnew, Dr. Julius Althaus, Mr. H. H. Dobree, and Mr. James M. Johnstone. The following will be the Friday Evening Meetings after Easter:—

April 26. John Hopkinson, M.A., D.Sc., F.R.S., "The Effects of Electric currents in Iron on its Magnetisation."

May 3. Veterinary Captain Frederick Smith, "The Structure and Function of the Horse's Foot."

May 10. The Hon. G. N. Curzon, M.P., "A recent Journey in Afghanistan."

May 17. Professor Walter Raleigh, "Robert Louis Stevenson."

May 24. J. Viriamu Jones, M.A., F.R.S., "The Absolute Measurement of Electrical Resistance."

May 31. The Earl of Rosse, K.P., D.C.L., LL.D., F.R.S., "The Radiant Heat from the Moon during the Progress of an Eclipse."

June 7. Professor Alfred Cornu, D.C.L., F.R.S., "Phénomènes Physiques des Hautes Régions de l'Atmosphère."

MEETINGS FOR THE WEEK.

Tuesday, 9th.—Institute of Civil Engineers, 8.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
Wednesday, 10th.—Pharmaceutical, 8.30.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1846.

THE SLIT OF A SPECTROSCOPE.

By WILLIAM CROOKES, F.R.S.

One of the most important parts of a spectroscope is the slit, and the best material wherewith to fashion the jaws has been the subject of much thought and experiment in my laboratory for some years past. The substance chosen must be very hard, and capable of being ground to a perfect knife-edge; it must not be granular in texture, or it cannot be worked to the required accuracy; it should not be brittle, or the cleaning which is occasionally necessary will be liable to break the fine edge, and it should be capable of standing any acid vapours to which it is liable to be exposed when left uncovered in a chemical lsboratory in active work; it must also not allow light to pass through except between the jaws, absolute opacity at every other part being imperative.

The following extracts from a letter I wrote to my friend Dr. Schumann, in May, 1893, will explain the difficulties, and how they were finally overcome:—

"You may feel interested in knowing the results of some experiments I have been lately making with the object of getting the best material for the jaws of the slit. I again tried iridium, using another piece of well-fused metal; but the old objection of granulation, when the knife-edge stage was reached, was as great as in the former instance. Pure wrought cobalt gives a fine edge, and is very hard and takes a good polish; if nothing better could be got, cobalt would do very well, but I do not know if it would stand the ordinary atmosphere of a laboratory for any long time without tarnishing. Manganese steel is even harder than cobalt, and from what I have seen will make as good an edge: but here the liability of tarnishing is still greater than in the case of cobalt.

"I have recently been making the jaws of my slit of transparent quartz, and I find this answer so perfectly that I cannot conceive anything better. Each jaw of the slit I am now making for the new spectrograph is 25 m.m. long, 13 m.m. wide, and 4 m.m. thick; it is bevelled off along one edge at an angle of 45°, thus:—

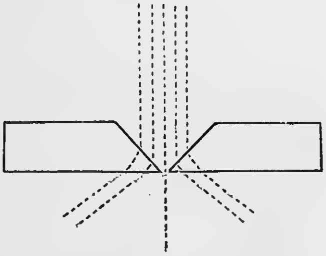


Fig. 1.

"The sides and angle must be ground true and polished. At first I had great difficulty in getting the knife-edge true. In the final grinding and polishing small splinters occasionally broke off the edge, and then I had to recommence the grinding and polishing to get rid of these little flaws. It is difficult for me to fashion a knife-edge of quartz at an angle of 45°. Ultimately I got over this difficulty by putting a very narrow bevel on the front of the plate, so making the angle of each jaw 90° (see fig. 2).

"You at once see that no light can get through the part of the quartz which is cut at an angle, owing to refraction, and the light coming through the flat part of the quartz plate can easily be stopped by a metal diaphragm or film of black varnish. The edge made in this way is absolutely black and opaque even in sunlight, and it will bear a high microscopic power without showing the least irregularity. I clean the slit from dust by opening it about half a millim., and passing a splinter of soft wood between the jaws. I have not yet put a micrometer to the quartz slit, but I see from preliminary experiments that I shall be able to work with a much narrower slit than I could if I used a metal one. It is very beautiful to see the absolute opacity and trueness of edge of one of these slits when examined under a high power."

I have now used nothing else but quartz jaws since the above quoted letter was written, and when properly made I consider them perfect. Besides quartz, several other hard crystals were tried. Sapphire makes good jaws, but being so hard there is corresponding difficulty in getting the edge true; it is also more difficult to get plates of sapphire quite transparent, and in this case perfect transparency is the essential for perfect opacity, for a transparent angle refracts all the light passing through it, and throws it on to the side of the tube, where it is cut off by a diaphragm, whereas a semi-transparent or cloudy crystal disperses some of the incident rays irregularly and makes the background of the image of the slit not absolutely black. In fine spectrum work any stray light illuminating the background is liable to obscure the visibility of faint lines. I tried an edge of a cut diamond, and it answered well, but quartz being hard enough, and so much easier to work, it is not necessary to go to harder crystals.

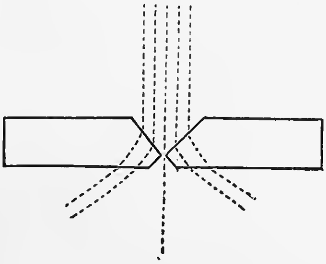


Fig. 2.

If the jaws are cut and polished by a lapidary, the workmen must be warned not to flatten the sharp edge to hide irregularities. I have had several jaws spoiled in that way. The flat face thus formed reflects incident rays, and those of them which are at a sufficiently acute angle to find their way down the tube to the collimator and prisms introduce false light and possibly false lines. The edges of the jaws must be quite straight, so that when they come together they cut off the light at once along the whole length of the slit. This is very difficult to secure, and is one of the reasons why I make the jaws from plates 25 m.m. long. The actual length of working slit not being more than one-quarter of that length it is easy to select sufficient from each jaw to get 5 or 6 m.m. of quite straight edge, even if the whole length is not perfect.

With the pair of jaws in the spectrograph at present in use I can take excellent photographs when they are only 0·0001 inch apart. For eye observations the width can easily be less than that.

Some advantage is gained by making the knife-edges of well-melted quartz. This material is tougher than the crystal and is not so liable to splinter. There is, however, a little difficulty in getting it free from air bubbles.

Formation-heat of Calcium Acetylide.—M. de Forcrand.—The heat sought $= +76{\cdot}95$ cal., setting out from solid calcium and gaseous carbon. —*C. R.*, cxx., No. 12.

NEW RESEARCHES BY PROF. RAMSAY ON ARGON AND HELIUM.

M. Berthelot announced, at a recent meeting of the Académie des Sciences, that he had received the following telegram from Prof. Ramsay:—

"Gas obtained by me:—Clèveite; mixture of argon helium. Crookes identifies the spectrum. Make communication to the Academy on Monday."

It appears from this telegram that Prof. Ramsay has made a new and very important discovery, that of a natural mineral containing argon—clèveite. This mineral has been discovered by Nordenskiöld, and consists of uranium oxide and of various rare earths.

In fact, the question concerns an entire group of compounds, known as *uraninites*, in which W. F. Hillebrand has mentioned the presence of an appreciable proportion of nitrogen, capable of being liberated by the influence of acids (*Bulletin of U. S. Geological Survey*, No. 78, 1891, pp. 43 to 79). He has made a special study of this singular reaction, which suggested to Ramsay the idea of a thorough examination. He has thus been led to detect, besides nitrogen, argon and helium.

In fact Ramsay recognises at the same time, in the gases extracted from clèveite, the presence of the spectrum ascribed to a hypothetical element, helium, which has been imagined to account for a special ray of the solar spectrum. Prof. Ramsay has thus discovered a compound of helium.

M. Berthelot, after the Session of the Academy on Monday, received the following letter from Professor Ramsay:—

"I have telegraphed to you to-day announcing the discovery of helium, the unknown element the yellow line of which exists in the solar spectrum.

"Whilst congratulating you on having succeeded in combining argon, I think it will interest you to learn how I have had the good fortune to make this discovery. Hillebrand (of Baltimore) has studied a rare mineral, clèveite. He was surprised to find that this mineral contained about 2 per cent of a gas, the spectrum of which he examined, and found it that of nitrogen. He caused the spark to strike through a mixture of this supposed nitrogen, with hydrogen in presence af sulphuric acid, and obtained ammonium sulphate. It has appeared to me extremely doubtful that any substance could give off free nitrogen after treatment with an acid.

"I took in hand the examination of this gas in the hope of finding a method of combining argon, since Hillebrand has remarked that there existed a definite relation between the nitrogen and the uranium oxide, which, along with lead oxide and rare earths, constitute this mineral.

"On causing the electric spark to strike through a mixture of this gas with oxygen in presence of caustic soda, I obtained a residue (the nitrogen is only present in a minimum quantity). This residue gave the spectrum of argon, and, in addition, another spectrum, the very brilliant yellow line of which does not coincide with the D line of sodium, though approximating to it. The wave-length, measured by my friend Crookes with his magnificent spectrometer, is 587·49.

"There are found, also, other lines less remarkable, in the red, the green, and especially in the violet. All these lines, except the characteristic yellow, have not yet been measured.

"Setting out from the red, and making a comparison with the spectrum of argon, I have found—

Red.—3 identical lines; 2 lines; 1 faint line; 1 line less faint; 1 line strong in He, faint in A.

Orange-red.—1 line equal in both; 1 line equal in both; 1 line equal in both; 2 faint lines.

Orange.—1 faint line; 3 rather strong lines.

Orange-yellow.—2 strong lines; 1 yellow brilliant line in He only (this is the characteristic line of helium); 7 green lines equal in both; 5 greenish-blue lines equal in both.

Green-blue.—1 faint line, not in argon; 1 brilliant line, not in argon.

Blue.—8 rather strong lines, not in argon.

Violet.—3 lines only in A; 2 lines in both, but stronger in A; 4 lines only in He; 2 lines only in both; 1 line only in both; three lines only in both; three lines only in both; 2 lines only in both.

"I have a rather large quantity of clèveite, and one of my assistants has already commenced extracting the gas in a large quantity. My task will be to separate the two substances, which will perhaps not be easy."—*Comptes Rendus*, No. 12, March 25, 1895.

REMARKS ON THE SPECTRA OF ARGON AND OF THE AURORA BOREALIS.

By M. BERTHELOT.

In a matter so novel as the study of argon it may perhaps be useful to suggest some approximating phenomena. From this point of view I take the liberty of mentioning the following:—

It is possible that the rays peculiar to the aurora may be due to a special form or compound of argon, or of elements still unknown, by which it may be accompanied. I request permission to recall a personal observation. During one of my recent experiments upon argon, performed in presence of the vapour of benzene, and with the exceptional circumstances of the rain of fire, there appeared at the ordinary pressnre in the entire extent of the tube a splendid greenish yellow fluorescence, characterised by a spectrum of remarkable rays and bands, and which recalled that of the aurora as far as I could compare them in the hasty conditions of my experiment.

There were perceived independently of the rays of hydrogen and the D rays, various rays—yellow and green, blue and violet—of which I will not fix the position on account of the feeble dispersion of the spectroscope, and the difficulty of comparing fluorescence spectra. I will confine myself to mention a brilliant ray close to the ray D, from which it is separated by a fine black absorption-ray and two groups of bands or broad rays, the one to the left of D in the orange, the other to the right in the yellow and the green, both furrowed by fine absorption-rays. The aspect of these bands was very analogous to that of the group of small rays shown to the left of E in Fig. 1 of Rayet's memoir "On the Spectrum of the Aurora" (*Journal de Physique*, i., p. 366, 1872). I showed these curious phenomena to the young *savants* working in my laboratory. Their analysis deserves to be compared with the spectra of the aurora and of helium.

This observation will thus explain the enigma of the aurora by the production of a fluorescent derivative of argon or of its family contained in the specimen sent me. Angström has already referred to fluorescence in his study on the aurora borealis.—*Comptes Rendus*, cxx., No. 12, March 25, 1895.

Extension to Magnesia of a Method of Synthesis of Fluorides and Silicates.—A. Duboin.—The author has obtained double fluorides of magnesium and potassium. He has found a method which gives well-crystallised products in the case of magnesia and glucina. He melts in a platinum crucible potassium fluoride obtained from the fluorhydrate of potassium fluoride at a bright red heat, and throwing into the melted salt calcined magnesia in small portions. The magnesia dissolves by degrees, as also does glucina. The product has the composition $MgF_2,2KF$. He has also isolated $MgO, K_2O, 3SiO_2$.—*Comptes Rendus*, cxx., No. 12.

A DEPHLEGMATOR FOR FRACTIONAL DISTILLATION IN THE LABORATORY.

By SYDNEY YOUNG, D.Sc., F.R.S., and
G. L. THOMAS, B.Sc.,
University College, Bristol.

Various forms of still-head have been devised for use in the laboratory (*vide* "Thorpe's Dict. of Applied Chem.," vol. i., p. 694), those of Wurtz, Linnemann, Le Bel, and Henninger and Glinsky being most frequently used.

Another form of dephlegmator, resembling in construction that employed in the Coffey still, has been recommended by F. D. Brown (*Trans. Chem. Soc.*, 1880, 49), but has not met with the attention it seems to deserve.

FIG I

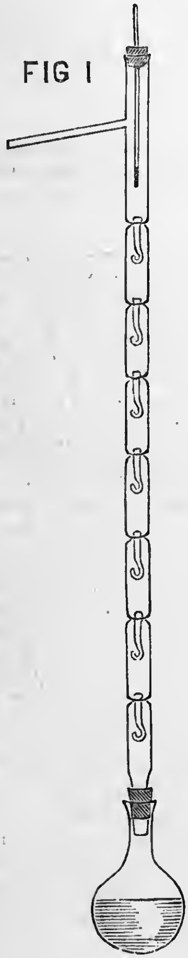
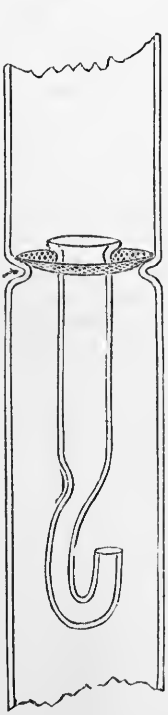


FIG 2



We have for some little time made use of a dephlegmator (Fig. 1) similar in principle, but differing from Brown's in construction; and as it has been found convenient, and has given very good results, we think that a description of it may be useful.

A glass tube, about 18 m.m. in internal diameter, is sharply constricted at intervals of about 8 c.m. (The constrictions may be formed by heating the tube, kept in regular and rather rapid rotation, with a small blowpipe flame, then producing a partial vacuum in the tube by drawing in with the breath). On the constricted portions of the tube rest discs of platinum-gauze, through the centre of which pass glass tubes of the form and dimensions shown in Fig. 2. The vapour passes through the condensed liquid resting on the platinum discs, and the excess of liquid flows down the tubes, resting on the discs.

While the distillation is proceeding, the pressure of the vapour forces the liquid up into the wider part of the dropping-tubes; if the tubes are too narrow above the head of liquid, there is danger of bubbles of vapour being caught and carried down, so as to empty the tubes, when the ascending vapour might find an easier passage through the tubes than the gauze. With the tubes constructed as shown in the diagram, this has never been found to occur.

As soon as the distillation is stopped, the level of the liquid falls to that at the lower end of the dropping-tubes, and this small quantity of liquid is easily recovered by removing the dephlegmator from the flask, and sending a small, but sharp, blast of air through the side tube.

In order to test the efficiency of the dephlegmator a mixture of 200 grms. of pure benzene and 200 grms. of pure toluene was distilled—(1) from an ordinary distillation-bulb with a still-head 30 c.m. long (from the bulb to the side tube); (2) from a flask with a plain still-head, 110 c.m. in length; (3) from a flask with a dephlegmator of the same length with seven constrictions.

The results are given in the table below:—

Temperature corr. to 760 m.m.	Weight of fraction in grms.		
	Short still-head.	Long still-head.	Dephlegmator.
80·2 to 83·2	0	0	36·5
83·2 ,, 86·3	0	1·2	99·6
86·3 ,, 89·4	9·0	48·4	22·3
89·4 ,, 92·5	99·4	94·4	20·3
92·5 ,, 95·6	86·9	51·8	18·8
95·6 ,, 98·7	54·8	36·3	19·5
98·7 ,, 101·8	35·8	30·6	15·1
101·8 ,, 104·8	30·0	26·4	5·3
104·8 ,, 107·9	30·9	22·0	18·9
107·9 ,, 110·3	53·0	51·9	36·5
110·3 ,, 110·9			40·1
Pure toluene 110·9°		36·2	66·1
	399·8	399·2	399·0

It will be seen that the separation with the long still-head is considerably better than with the short one, but that neither of the plain still-heads can compare at all in efficiency with the dephlegmator.

After three additional fractionations with the dephlegmator, 175 grms. of pure toluene and 60·8 grms. of pure benzene were recovered; two further fractionations of the partially purified benzene brought up the weight of the pure substance to 174·4 grms. The weight of each pure substance recovered amounted, therefore, to over 87 per cent.

We are at present using a dephlegmator 125 c.m. long with twelve constrictions, the flask being supported by a retort-stand and clamp on the floor and the condenser on the working table.

ON THE
PROPERTIES OF AMORPHOUS SILICON.

By M. VIGOUROUX.

In a former paper we have indicated that it is possible, under certain conditions, to reduce silica by magnesium, and to obtain an amorphous silicon quite free from foreign bodies. The properties of this substance are as follows:—

Physical Properties.

It is a fine powder, of a maroon colour, and adheres to any moist or rough surface. It readily absorbs gases and watery vapour, and requires for their expulsion to be heated to near redness; its mean specific gravity at 15°

is 2·35°. It may be melted and easily volatilised in the electric furnace. It is soluble in a great number of metals in a state of fusion.

Chemical Properties.

It does not seem to be affected by heat. It has been practicable to raise it for a long time to high temperatures without any alteration in its properties, which depends on the strong heat liberated at the moment of its preparation. Hydrogen has no action. Fluorine attacks it at common temperatures.

In chlorine silicon ignites at 450°, and in bromine about 500°; in iodine there is neither incandescence nor apparent reaction.

In the oxygen of the air there is superficial oxidation without incandescence. In pure oxygen there is brisk combustion about 400°, and the heat is such that the silicon formed is melted.

In sulphur incandescence occurs about 600°. In nitrogen it does not react below 1000°; at a higher temperature it attacks. In silicon it forms an amorphous nitride. Phosphorus, arsenic, and antimony, if heated with it, distil without reactions. Carbon and boron act only in the electrical furnace. The metals seem not to combine with silicon at temperatures generally available in laboratories. Magnesium alone yields a silicide with lively incandescence.

Dry gaseous hydracids attack it slowly about dull redness. Hydrogen sulphide, if gradually heated up to its dissociation-point, does not act upon the silicon. Ammonia is decomposed at cherry-redness; hydrogen is liberated and the nitrogen combines with the silicon, forming a nitride.

Watery vapour is decomposed at the same temperature, forming silica and hydrogen, which escape. The decomposition is continuous, but slow. Sulphurous anhydride, if passed over silicon at about 1000°, is not reduced. Nitrous and nitric acid act slowly towards 800°, with fixation of nitrogen and oxygen. If the reaction is lively there is incandescence. Phosphoric anhydride is reduced with incandescence before a red-heat. It is the same with the oxygenc ompounds of arsenic and antimony. Between 800° and 1000° carbonic anhydride is reduced to the state of carbon monoxide. The latter is not attacked even at 1200°. Silicon is not attacked by any acid dissolved, or liquid, if acting alone, nor by fuming nitric acid heated to ebullition, nor by sulphuric acid concentrated and boiling, nor by concentrated hydrofluoric acid if heated with it to 100°. The combined action of two acids, or of an acid and another body, is often effective. Thus aqua regia at 100° acts in course of time, and ultimately transforms it into anhydrous silica. A mixture of nitric acid and hydrofluoric acid attacks it at the common temperature with an escape of muddy fumes and of silicon fluoride. Hydrofluoric acid, mixed with potassium nitrate or chlorate, acts with violence; it is the same with ordinary nitric acid if mixed with potassium fluoride.

Silver fluoride is decomposed with incandescence before a red-heat; there are formed silicon fluoride and silver, which is set at liberty, and is found in small melted grains. It is the same with zinc and lead fluorides, &c.

Most oxides are reduced in glass tubes heated with a Bunsen burner, in many cases with incandescence; such are mercury, copper, lead, bismuth, tin, iron, manganese oxides, &c. The alkaline and alkaline earthy oxides are attacked energetically.

Hydrofluoride of potassium fluoride seizes the silicon and liberates hydrogen. Lead sulphate and calcium phosphate are reduced. The silicon may be thrown upon potassium chlorate in decomposition without incandescence, but this phenomenon occurs if the two substances are intimately mixed and then heated. Potassium nitrate reacts only at its decomposition temperature. The alkaline carbonates, whether in solution or fusion, convert it into silica. Certain oxidising agents, such as potassium dichromate and lead chromate, are decomposed with incandescence and explosion below a red-heat. The mixture of fuming nitric acid and potassium chlorate has no appreciable action.

The amorphous silicon obtained by reducing silica with magnesium corresponds neither to the amorphous varieties α or β of Berzelius. It approximates rather to crystalline silicon. Nevertheless the latter has hitherto been regarded as incombustible in oxygen. This indifference is only apparent. If we raise the temperature abruptly, the crystalline silicon ignites at 400° in oxygen, and burns with a dazzling lustre. If it is finely powdered the combustion may be complete.—*Comptes Rendus*, cxx., p. 367.

THE CHEMOMETER.*

By W. OSTWALD.

(Concluded from p. 168).

In like manner, it may be shown that the differences of the chemical and electrical potential must increase or decrease in the same direction. For this purpose we only need suppose the existing differences of chemical and electrical intensity, compensated by a suitable number of circuits introduced, and to apply the above conclusions.

We may, therefore, accept the result as certain, that, in fact, the electrometer may serve as a chemometer. The question now arises as to the extent in which this process is applicable. Since it is connected with the fact the chemical process is proportional to the electrical, the presence of electrolytes is a necessary condition of the method. As to what minimum of electric conductivity we can go depends on the question, With how little electricity the electrometer can act? It is now a peculiarly favourable circumstance that the quantities of electricity adhering to the ions are extremely large, so that quantities of matter far beyond the limits of the ponderable can yield quantities of electricity very sufficient to set the electrometer in action. We may, in fact, in this direction complain rather of too great than of too small sensitiveness. On the other hand, it is certain that the sphere of electrolytes extends very much beyond the aqueous solutions of acids, bases, and salts. A relatively great number of organic compounds may be, without doubt, appended to the ordinary electrolytes. It is here also a question of continued experimental elaboration to extend the process gradually further and further. Even that which is already accessible will require for its experimental elaboration the work of a number of years.

Finally, I must advance another question. Electric energy is only one of those which accompany chemical changes; but as we always see changes of volume, or in solutions variations of osmotic pressure, connected with chemical reactions, we must conclude that also the energy of volume may furnish aids to the measurement of chemical potential or of affinity. Indeed, if we reflect that the modern theory of chemical circuits refers their action everywhere to the activity of osmotic pressures, *i.e.*, to the changes of volume energy, we find in the latter the fundamental inseparable from the chemical process, whilst for obtaining chemical energy as electrical we always require peculiar arrangements.

In fact, for a great number of chemical reactions we may carry out perfectly similar considerations in which pressure plays a part similar to that of electromotive force. We know also that for solutions and gases the magnitude of capacity is proportional to the energy of volume and the volume is proportional to the magnitude of chemical capacity, and for quantities comparable (the molecular weights) is equal in magnitude. There appear, also, relations quite similar to the foregoing, though with a difference very essential for the experimental phase of the

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* From the *Zeitschrift fur Physikalische Chemie.*

question. The free, or changeable, electricity is simply equal to the product of the quantity of the electricity into the difference of potential, and the latter is the measure of the same, as the former, according to Faraday's law, is alike for quantities of different substance which are chemically equivalent. The volume energy, on the contrary, appears in the only case hitherto accessible, that of volumes and gases, as the product of the volume into the difference of the logarithms of the two pressures. For equal differences of the chemical potential the pressures increase, not in an arithmetical, but in a geometrical, series, and soon arrive in a region inaccessible to measurement.

To take an instance. If a difference of the chemical potential expressed electrometically by 1 volt, correspond in the most favourable case to the relation of two pressures, the one 10^{17} times greater than the other. If we take as the smallest measurable pressure $\frac{1}{1000}$ of an atmosphere, the other would amount to 10^{14}, *i.e.*, 100,000 millions of atmospheres, whilst our means of measurement scarcely exceed 1000 atmospheres. As, moreover, chemical potentials have been measured up to three or four volts in electrical measure, we arrive at the quite inconceivable values of 10^{48} or 10^{65} atmospheres, which we require, in the most favourable case, to ascertain what the electrometer tells us without any difficulty.

SYNTHETIC EXPERIMENTS IN THE PYRAZOL SERIES.*

Part I.

By R. von ROTHENBURG.

(Concluded from p. 165).

Hydrazin seems to form a pyrazolidon with cinnamic acid, as the oily product here also takes a transitory blue-green product with nitrous acid.

On Pyrazololidon.

This compound cannot be obtained by the action of equal mols. of hydrazin hydrate and malonic ester. On the contrary, malonic ester and hydrazin form the readily soluble malonhydrazidic acid, which on heating forms pyrazololidon with abscission of water and the closure of the ring.

It is obtained as follows:—Equal mols. hydrazin hydrate and malonisteric acid are mixed, after dilution, with 3 vols. alcohol to prevent a too violent reaction. The mixture is then boiled for half an hour and distilled from the oil-bath. At 195—205° there passes over a yellow oil of an intense odour. The sparingly soluble dimalonylhydrazin was not present in the mixture even before distillation.

Ferric chloride colours the new substance violet-blue; it dissolves in alkali with a yellow colour; as also readily in water, especially hot, and in the usual solvents. Strong mineral acids and alkali split off hydrazin on brisk ebullition.

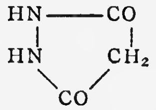
(4)-Benzal-pyrazololidon.—With benzalaldehyd there is formed a reddish yellow condensation-product, the properties or which offered no guarantee of purity.

(4) - Isonitroso - pyrazololidon is formed on passing nitrous acid into the aqueous solution of pyrazololidon, and dissolves very readily with a lemon-yellow colour. On mixture with ammonia and silver nitrate, and subsequent careful neutralisation with acetic acid, there is deposited the lemon-yellow compound, (4)-Isonitroso-pyrazololidon silver.

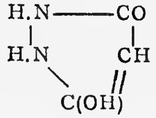
Pyrazololidon-(4)-*p*-azotoluol is obtained by the ordinary method for preparing the azo-derivatives of the pyrazolons, taking especial care for good refrigeration. The bright reddish yellow colouring-matter is precipitated by acids. This strongly acid substance is much yellower than the corresponding compound of pyrazolon. It is decidedly more soluble in organic solvents, and crystallises from glacial acetic acid in small, shining, yellow-red crystals, fusible above 250°.

Constitution of the Pyrazololidons. Isomerism and Tautomerism of the Pyrazololidons. Course of Reaction, and Conditions of their Formation.

The pyrazololidons have the general formula—

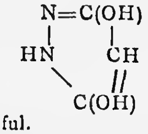


with the tautomerous by-form analogous to the pyrazolons:—



with which the behaviour with diazo-salts and the circumstance that the metallic salts contain only 1 equiv. of metal agree perfectly.

Whether there exists also a second pseudoform—



must remain doubtful.

The pyrazolidons arise from derivatives of bibasic acids in which both carboxyls are linked to a single carbon atom. A condition of this formation is that both the carboxyl-groups possess a differently intense capacity of reaction with hydrazin, as there are otherwise formed symmetrical di-substitution products.

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.*

By AMOS PEASLEE BROWN.

(Concluded from p. 172).

The important point brought out in these experiments is that pyrite contains a large amount of ferric iron, while in marcasite the iron apparently exists in the ferrous condition. Some reducing action might, however, have taken place, due to the sulphides formed. The condition of the iron in the chlorides found in the boat and tube was very carefully tested by several reagents in each case, and there can be no doubt as to the correctness of the results as stated above.

The decomposition of the sulphides by metallic salts seemed to offer some hope of being productive of results that would show in a quantitative way the exact amounts of ferrous or ferric iron that are present in these two minerals. In this line, the action of gold chloride, silver nitrate, and silver sulphate were tried in a qualitative way with both minerals. Of these the first gave a ready decomposition with both, and produced both ferrous and ferric salts in each case. The silver nitrate gave a similar result. Silver sulphate acted very slowly and without any definite results.

The action of copper sulphate in neutral solution and under pressure was tried with very remarkable results.

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* From the *Journal Praktische Chemie.*

* Read before the American Philosophical Society, May 18, 1894 —From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

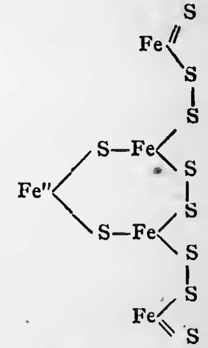
At the ordinary temperature and pressure the solution of this salt has little effect on either mineral, and the same is true of the solution at a boiling temperature, but under pressure the reaction is complete. The experiment was conducted as follows:—0·2 grm. of the finely pulverised mineral was introduced into a stout glass tube, and 50 c.c. of a 10 per cent solution of the salt, $CuSO_4.5H_2O$, added, the air displaced with a pinch of $NaCO_3$, and a drop or two of H_2SO_4 (dilute), and a heavy seal made on the tube. The tubes containing the two minerals were heated for six hours in an autoclave to a temperature of about 200°. The contents of the tubes were found to contain no traces of undecomposed mineral, but there was a black, more or less flocculent precipitate in its place. This proved to be copper sulphide. The solution had not altered appreciably in appearance. The liquid contents of the tube were in each case transferred to a flask previously filled with CO_2 and with 10 c.c. dilute sulphuric acid in the bottom, the tube then rinsed with water and the amount of ferrous iron present titrated with freshly standardised potassium permanganate. In the case of marcasite this gave 18 c.c. $KMnO_4$ solution (this was two- or three-tenths of a cubic centimetre too much, on account of the difficulty in catching the end-reaction). To correct this for the iron in the copper sulphate, a blank of 50 c.c. $CuSO_4$ solution, the same as used above with 10 c.c. dilute sulphuric acid, was titrated with the permanganate, giving 0·5 c.c. reduction. The factor of the permanganate was 0·0054 grm. Fe for 1 c.c. Making the correction for the reduction of 50 c.c. $CuSO_4$ solution, this gives 47·25 per cent of iron in solution as against 46·67, the theoretical amount in FeS_2. No doubt if the end reaction had been more exact there would have been a still closer correspondence in the result.

The tube containing the pyrite was treated in exactly the same manner, and gave a reduction of permanganate of 3·8 c.c. This time the end reaction was sharp and exact. Calculating the above to iron (after making correction for $CuSO_4$) this gives 8·91 per cent of ferrous iron in pyrite. As the total iron is 46 67, this corresponds to 19·09 per cent of the iron in the mineral, or almost exactly one-fifth. These experiments demonstrate in a positive manner the condition of the iron in the two minerals, and even show the exact amounts of each condition of the iron, ferrous and ferric.*

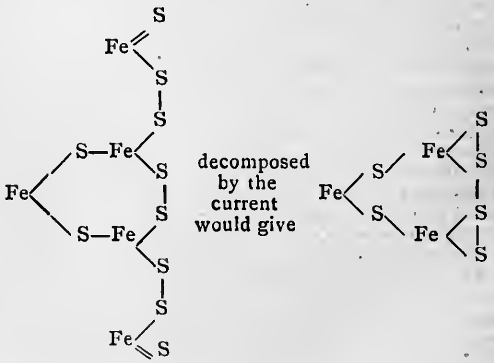
That marcasite should hence be be more readily decomposed by oxidation than pyrite seems fully explained by the foregoing investigations, as it consists of $Fe''S_2$, an unsaturated compound. In this compound sulphur must link to sulphur, or the compound have unsaturated bonds, and hence any element which would attack the sulphur would break up the compound. On the other hand, the iron is held to the sulphur by its full number of bonds, and any substance that has an affinity for iron could not so readily attack it in this condition, This would be true whether ferrous iron be considered here as Fe_2, with a valence of four, or as Fe''. That marcasite is $Fe''S_2$ is also indicated by its oxidation in the air into $FeSO_4$ mainly. Under these same conditions it will be noted that pyrite forms both ferrous and ferric compounds, as $FeSO_4$, but much more $Fe_4O_3(OH)_6$ and free sulphur. Marcasite, however, when decomposed by water under pressure (in nature) forms much limonite also, this being due no doubt to the oxidation being effected under pressure. This constitution explains also the fact that the oxidation of marcasite is continuous and complete, as shown by the current oxidations. It will be shown also that this constitution of pyrite that has been made out explains fully its action with the current. That marcasite is unsaturated is also indicated by the fact that it has not been made artificially or at any rate positively identified in any of the artificial FeS_2 that has thus far been made. If marcasite be a persulphide, as its formula would seem to indicate for a ferrous compound, none of the methods detailed above for making FeS_2 would be applicable in its case, unless perhaps the method of Deville might produce it. All of the other methods would probably produce ferric iron, at least in large part, and the resulting product would be pyrite.

The formula for pyrite derived from my investigations and expressing the relation of the two conditions of the iron in the simplest way is $4Fe^{iv}S_2{\cdot}Fe''S_2$. This formula is also borne out by what we know of the formation of pyrite as given in the early part of this paper, and by such experiments as I have made on its decomposition, as well as the fact above alluded to, that it, in oxidising in nature, does not form much ferrous compounds, but mainly ferric. And it also explains the fact that it is more stable as regards any element attacking its sulphur, for it is most probable that all the sulphur of the $Fe''S_2$ in its formula is linked to iron. I would propose the following structural formula, not as expressing the exact constitution of the compound, for of that we know nothing, but as an expression of the condition of the iron in the molecule and as embodying in a quantitative way the result of my investigations into its constitution. It will be noticed that the sulphur of the $Fe''S_2$ is made to link entirely with iron.

Structural formula of pyrite.



If ferric iron be considered as Fe^{iv}—Fe^{iv} it is only necessary to connect the ferric Fe atoms with bonds, but it seems to me that ferric iron is more likely Fe''', and at any rate this is the simplest way to regard it. A very striking proof of the correctness of the idea expressed in this structural formula that $Fe''S_2$ in pyrite has its sulphur all linked to iron is afforded in the experiments on oxidation of the mineral by means of the electric current as detailed above. It will be recalled that the amount thus oxidised was between 21 and 22 per cent. Now if two molecules of FeS_2 be split off from the above formula, say those linked by sulphur to sulphur, there would remain a saturated compound much more difficult to decompose (theoretically) than the pyrite molecule illustrated, and the amount of sulphur thus removed would be by calculation 21·33 per cent. This action could be thus illustrated.



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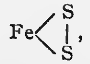
* These results have been confirmed by experiments made during the past year in this laboratory, and not yet published.

Of course this structural formula is only intended to represent the probable relations of the atoms in the molecule, and the probability that the Fe″S_2 is entirely saturated.

A structural formula for marcasite might be given as—



and this really expresses our entire knowledge of its constitution. It may be any polymer of this, for being unsaturated it should be capable of forming polymers.

I much regret that want of time has compelled me to discontinue these latter investigations into the decomposability of these minerals by solutions of metallic salts under pressure, as it seems to open up a way for the study of many other sulphides, and would doubtless be productive of most valuable results. Besides this, it would probably adduce additional proof of the correctness of my formulæ for these minerals as given above.

Acknowledgment.

I take this occasion to express my sense of gratitude to Prof Edgar F. Smith, who suggested the work to me, and who, by his constant encouragement and ready advice, has greatly furthered its prosecution. Many of the experiments were made at his suggestion, and no doubt the success of the work is largely due to him.

NORTH CAROLINA MONAZITE.*

By H. B. C. NITZE.

Monazite is a phosphate of the rare earths cerium, lanthanum, and didymium. It also contains thoria and silica, which are present in varying percentages. The mineral is subtranslucent, light yellow, or yellowish brown or green, and has a resinous lustre. Its hardness is from 5 to 5·5, and its specific gravity 4·9 to 5·3. Its economic value lies principally in thoria, which it contains; this is used as one of the constituents in the manufacture of mantles for the Welsbach and other incandescent gas lights.

The mineral is somewhat widely distributed, but has been found in commercial quantities only in Brazil, Siberia, Norway, and North and South Carolina in this country. The North Carolina area embraces between 1600 and 2000 square miles, situated in Burke, McDowell, Rutherford, and Cleveland counties. The principal deposits of this region are found along the waters of Silver, South Muddy, and North Muddy creeks, and Henry and Jacob's Forks of the Catawba river in McDowell and Burke counties; and the Second Broad river in McDowell and Rutherford counties; and the First Broad river in Rutherford and Cleveland counties. Some monazite is also found in Polk county, and along the western edge of Catawba, Lincoln, and Gaston counties.

The best crystallised specimens have been found at Milholland's Mill and Stoney Point in Alexander county. The monazite occurs in the sands and gravels of the stream-beds, associated with other minerals, such as quartz, felspar, hornblende, epidote, mica, magnetite, garnet, zircon, rutile, corundum, &c. The primary source of monazite is in the crystalline gneisses and schists, of which it is an accessory constituent. The material produced from the disintegration of the decomposed country rock is deposited in the stream-beds, and undergoes, by virtue of a continual current and differences of specific gravity, a natural process of partial sorting and concentration. The richer portions of the stream deposits are thus, as a rule, found near the head-waters.

As the percentage of thoria is variable in different sands, the value of the mineral consequently varies accordingly, and must be determined by careful chemical analysis. Some monazite contains practically no thoria. It is stated that the transparent greenish and yellowish brown varieties are usually the richest. The best north Carolina sands (highest in thoria) occur near Brindletown, Burke county, and in the northern part of Cleveland county. Some of the highest grade Brindletown sand runs from 4·00 to 6·60 per cent of thoria; sand from Gum Branch in McDowell county is reported to run 3·30 per cent thoria; some sand from near Shelley in Cleveland county contains 2·76 per cent thoria.

The thickness of these stream-gravel deposits is from 1 to 2 feet, and the width of the mountain streams in which they occur is seldom over 12 feet. The sluice-boxes used in separating it are about 8 feet long by 20 inches wide by 20 inches deep. Two men usually work at a box, the one digging the gravel and shovelling it into the box, the other one working it up and down in the box with a gravel-fork or perforated shovel in order to float off the lighter-sands.

These boxes are cleaned out at the end of the day's work, the cleaned monazite being collected and dried. If it contains magnetite it is treated with a magnet. It is then ready for packing and shipment. From 20 to 35 lbs. of cleaned monazite sand, per hand, is considered a good day's work. The value of the best grades of sand is 6 to 7 c. per pound at the diggings.

During the past two years the following shipments of monazite sand have been made from this region:—

In 1893: 110,000 lbs. at 6 c. at mines, 6600 dols.; 20,000 lbs. at 5 c. at mines, 1000 dols.; total, 130,000 lbs., 7600 dols. In 1894: 460,000 lbs. at 6¾ c. at mines, 31,050 dols.; 80,000 lbs. at 6 c. at mines, 4800 dols.; 6855 lbs. at 5 c. at mines, 342.75 dols.; total, 546,855 lbs., 36,192.75 dols.

THE CAUSE OF LUMINOSITY IN THE FLAMES OF HYDROCARBON GASES.*

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

In a paper read before the Chemical Society in 1893, I showed that in the inner non-luminous zone of a flame of ordinary illuminating gas, the hydrocarbons originally present in the gas, and consisting of ethylene, butylene, benzene, methane, and ethane, became converted by the baking action of the walls of flame between which they had to pass into acetylene, and that, at the moment when luminosity commenced, over 80 per cent of the total unsaturated hydrocarbons present consisted of this compound.

The presence of acetylene at the point where luminosity commenced naturally suggested that it was in some way due to actions in which the acetylene played the principal part—either that it split up into carbon and hydrogen under the influence of heat, and so supplied the flame with the solid particles necessary, according to Sir Humphry Davy's theory of the cause of luminosity, or else by its polymerisation it formed the dense vapours required by Dr. E. Frankland's more recent hypothesis.

In order to elucidate this point, I carried out the long series of experiments upon the action of heat upon flowing ethylene and other hydrocarbons, which formed the subject of communications to the Royal Society in 1893 and early this year, in which I showed that whilst flowing through a heated area (the temperature of which was between 800° and 1000° C.), ethylene decomposed according to the equation—

$$3C_2H_4 = 2C_2H_2 + 2CH_4.$$

and that the acetylene then polymerised into a large

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* Read at the Sixty-Eighth Meeting of the American Institute of Mining Engineers, Florida.—From the *Engineering and Mining Journal.*

* A Paper read before the Royal Society.

number of more complex hydrocarbons, amongst which benzene and naphthalene were conspicuous, whilst at temperatures above 1200° C. no polymerisation took place, but the acetylene formed from the ethylene decomposed at once into carbon and hydrogen, whilst the methane, which up to this temperature had been but little affected, decomposed into—

$$2CH_4 = C_2H_2 + H_2,$$

and this fresh supply of acetylene at once broke up to carbon and hydrogen, so that at temperatures above 1200° C. the complete action might be looked upon as being—

$$C_2H_4 = C_2 + 2H_2.$$

These results have an important bearing upon the cause of the luminosity in the flame, as it is manifest that if the temperature of the luminous zone is above 1200° C., the light emitted must be due to incandescent particles of carbon, and not to incandescent hydrocarbon vapours.

On determining the temperature of an ethylene flame whilst burning from a small fish-tail burner by means of the Le Chatelier thermo-couple, used in the way described in my paper (*Chem. Soc. Journ.*, 1893) on the luminosity of coal-gas flames, I found that the temperatures were as follows:—

Portion of Flame.	Height above Burner.	Temperature.
Non-luminous zone	½ inch	952° C.
Commencement of luminosity	1¼ "	1340
Top of luminous zone ..	2 "	1865
Sides of " " ..		1875

Showing that luminosity commenced at 1340° C., and continued even at 1875° C., temperatures at which the incandescent vapour theory becomes untenable.

It might be urged that the heavy hydrocarbons already produced at a lower temperature in the non-luminous zone are not so easily decomposed by heat as acetylene, and that these may be causing the luminosity, even though carbon particles be present from the decomposed acetylene; but this would hardly be possible, as so little besides acetylene is to be found at the top of the non-luminous zone of an ethylene flame, and it can be experimentally shown that, even when benzene vapour is formed and is largely diluted, it begins to break up and deposit carbon at 1200° C.

The supporters of the "solid particle" theory of luminosity agree in concluding that the liberated carbon, existing as it does in a condition of molecular division, is heated to incandescence partly by its own combustion, and partly by the combustion of the hydrogen and carbon monoxide going on around the finely-divided carbon particles.

As has been pointed out by many observers, it is clear that the carbon particles themselves undergo combustion, otherwise they would escape unburnt from the flame, whilst it is manifest that the combustion of hydrogen and carbon monoxide, which plays so important a part in the flame, must add its iota to the temperature attained by them.

Both these sources of temperature, however, would be manifest in the flame itself, and with flames of given size burning from the same description of jet we ought to find that their luminosity is governed by—

A. The temperature of the flame.
B. The number of carbon particles in a given area.

Moreover, we should expect that the higher the temperature of the flame, the whiter would be the light emitted, so that a comparatively low temperature flame, even when rich in carbon particles, would be yellow and lurid as compared with a flame containing the same or a smaller number of particles, but which had a higher temperature.

It has been pointed out by Prof. A. Smithells (*Phil. Mag.*, 1894, p. 249) that it is erroneous to consider the temperature of a flame as being the temperature recorded by thermometric instruments inserted into the flame, as by such devices you only obtain the mean temperature of a considerable area of the flame uncorrected for loss from conduction.

It is also perfectly well known that in a flame a thick platinum wire may only be heated to redness, whilst a thin wire may even be fused; and this suggests that flame temperatures taken by the Le Chatelier thermocouple of platinum and platinum-rhodium wires may be totally incorrect. In using this beautiful and convenient device, I have found that the length of the wires twisted together made practically no difference in the recorded temperature, and that one twist was as good as six.

In all my flame experiments I have made the twist as short as possible, and, by always using wires of the same thickness, have obtained results which are at any rate comparable if not correct; and in order to find what difference the thickness of the wires would make, I got Messrs. Johnson and Matthey to draw for me wires of 0·018, 0·011, and 0·003 of an inch diameter, and having calibrated the galvanometer scale for temperature with thermo-couples of the same length of twist made from each of them, obtained the following results with the same portion of a Bunsen flame.

Wire used.	Temperature shown.
0·018	1617° C.
0·011	1728
0·003	1865

These results show that the diameter of the wire seriously affects the temperature recorded under these conditions by the thermo-couple, the same degree of heat being recorded by the fine wire as being 248° hotter than is shown by the thickest wire employed, this discrepancy being probably chiefly due to loss by conduction,

In taking the temperature of heated gas flowing through a tube this source of error is but small, as, some considerable length of wire being heated on each side of the twist, conduction has but little effect on the thermo-couple itself; but in determining the temperature of flames it is manifest that the finest usable wire must be employed in order to reduce the error from conduction. Test experiments also showed that no part of the thermo-couple must project beyond the flame, as if it did a considerable diminution in the recorded temperature took place.

For these reasons it was manifestly best to use the finest wire which could be employed without the risk of fusing at the temperatures existing in the flames to be tested; and all temperatures recorded in this paper were made with wire 0·011 inch in diameter, the twist being as short as possible, so that it is probable that, although the temperatures may be from 100° to 200° too low, yet the results are strictly comparable.

Experiments which I have lately made with pure acetylene, prepared by the action of water upon calcic carbide, shows it to be the most powerful illuminant to be found amongst the gaseous hydrocarbons, as when burnt in a small flat flame burner under the most suitable pressure, and its illuminating power calculated to a flow of 5 cubic feet an hour, its value is equal to about 240 candles.

The colour of the flame is pure white, and an ethylene flame beside it looks yellow and dull—the purity of the light at once suggesting a very high condition of incandescence in the particles of carbon present in the flame.

On now taking the temperature of the various portions of the flame, and comparing these with the temperatures obtained in the same way with the ethylene flame and a coal-gas flame of the same size, the following results are obtained:—

Portion of Flame.	Acetylene.	Ethylene.	Coal Gas.
Non-luminous zone ..	459° C.	952° C.	1023° C.
Commencement of luminosity	1411	1340	1658
Near top of luminous zone	1517	1865	2116

whilst the illuminating value of the gases calculated to a flow of 5 cubic feet an hour in the burners best suited for their consumption are—

Acetylene	240·0
Ethylene	68·5
Coal gas	16·8

whilst if all were compared when burning from flat-flame burners of the same size as those in which the temperatures were determined, the results, when calculated to a consumption of 5 cubic feet an hour, would be—

Acetylene	211·0
Ethylene	31·5
Coal gas	nil.

Here, then, we have the anomaly of three gases, which not only do not conform to the preconceived expectation, but which have their ratio of temperature and illuminating value directly opposed to each other.

In the case of the acetylene and ethylene, moreover, the molecules contain the same number of atoms of carbon, and yet we obtain so enormous a discrepancy in their illuminating value.

The fact that there is no apparent relation existing between the temperature of the flame, or the probable number of carbon particles contained in it and its illuminating value, at once suggests that the luminosity must be in great part governed by some thermo-chemical changes taking place in the flame itself, and which do not of necessity affect the average temperature of the flame to any great degree.

The researches of Hittorf (*Wied. Ann.*, vii., pp. 587, 591) and Siemens show that air, steam, and the oxides of carbon, even when heated to temperatures above those existing in luminous hydrocarbon flames, are perfectly non-luminous; and the fact that the Bunsen flame, when supplied with sufficient air, has a temperature exceeding 1800° C. in its hottest part, and yet emits no light, shows us that it is exceedingly unlikely that any interactions leading to luminosity take place amongst these ordinary flame gases.

The fact that most of the unsaturated hydrocarbons in the flame are converted into acetylene before luminosity commences, naturally draws one's attention to this body, and the fact that it is highly endothermic at once suggests the idea that it may be the liberation of heat during its decomposition that endows the carbon particles produced from it with an incandescence far higher than any which could be expected from the temperature of the flame.

Berthelot has calculated that the temperature developed by the detonation of acetylene at constant volume is no less than 6220° C., and if this be imparted at the moment of its liberation to the products of its decomposition, the incandescence of the carbon particles is at once explained.

If luminosity be even partly due to this cause, the detonation of pure acetylene first recorded by Berthelot should develope light, and, in order to see if this were so, a thin glass tube, closed by a cork, had a detonator containing one-tenth of a grm. of mercuric fulminate suspended in it by two copper wires, which were connected by a thin platinum wire in contact with the fulminate, and on firing the detonator by the electric current the flash of the fulminate was found to emit but a feeble light.

The same charge was fixed in a similar tube filled with pure acetylene collected over mercury, the result being a flash of intense white light and the shattering of the tube, the pieces of which were thickly coated with the carbon produced by the decomposition of the acetylene.

Moreover, the small piece of white tissue paper used to contain the fulminate was only scorched at the points where the explosion of the fulminate had burst through it, showing that in the instantaneous decomposition which had taken place the intense heat which had been developed either was confined to the products of decomposition, or else had hot had time to scorch the paper.

The experiment at first sight seemed conclusive evidence that it was the endothermic nature of the acetylene which, during its decomposition in the flame, endowed the particles of carbon with the necessary incandescence, but the objection presented itself that, when exploding mixtures of oxygen and hydrogen in the eudiometer, a distinctly luminous flash is produced, and, although the light so obtained is feeble as compared with the intensity of the white light produced by the detonation of the acetylene, still further proof is necessary before this action can be accepted as the prime factor in producing luminosity.

It is also manifest that it would not do to assume that the rapidity of the decomposition of the acetylene in a flame was nearly so great as when the undiluted gas was detonated, and the question arose as to whether it would be possible to obtain evidence as to acetylene, when exposed to heat alone, liberating carbon in a luminous condition.

Although the instantaneous liberation of heat on the decomposition of the gas by detonation appears to confine the temperature to the products of its decomposition, it was to be expected that, on being decomposed by heat, and probably, therefore, at a slower rate, the increase in temperature might be detected.

To try this, pure acetylene was passed through a platinum tube, 2 m.m. in diameter and 40 c.m. long, in which the Le Chatelier thermo-couple was arranged as follows:—The two wires were twisted together for a length of 3 m.m., and the wires on either side of the twist are then passed through thin glass tubes, which are fused on to them; having been in this way coated with glass so that only the twist is exposed, they are passed through the platinum tube, the glass insulating the wire from the metal of the tube, and also keeping the thermo-junction in such a position that it registers the temperatures of the gas in the tube, not that of the wall of the tube. To each end of the platinum tube glass T-pieces are fitted, down the stems of which the wires pass to mercury seals; from the metal seals conducting wires lead to the resistance-coils, the key, and a reflecting galvanometer.

A steady flow of acetylene was allowed to pass through the tube, and was led into water at the other end. The tube was slowly and carefully heated for about 4 inches of its length, and, as the temperature reached 700° C., white vapours began to flow from the tube, and these, as the temperature rose, increased in quantity. The source of heat had been so regulated that the temperature had risen about 10° per minute, but, almost immediately 800° C. was passed, the galvanometer registered a sudden leap up in temperature to about 1000° C., whilst finely-divided carbon poured from the tube. This seemed to indicate that 800° was about the temperature at which the pure acetylene broke up into its constituents, and an experiment was now made to see if this developed incandescence in the liberated carbon.

(To be continued).

NOTICES OF BOOKS.

Chemical Analysis of Oils, Fats, Waxes, and of the Commercial Products derived therefrom. From the German of Professor Dr. R. Benedikt. Revised and Enlarged by Dr. J. Lewkowitsch, F.I.C., F.C.S. 8vo., pp. 683. London and New York: Macmillan and Co. 1895.

We generally look with distrust upon foreign scientific books rendered into English by a foreigner, since, though fully understanding the original, he is in general not sufficiently acquainted with the resources of our tongue. The instance before us forms a signal exception. We find in it nothing which might not have come from the pen of an educated Englishman.

Dr. Lewkowitsch refers to the wearisome prolixity of

Continental chemists in describing analytical processes. This fault is as largely indulged in by American writers.

Passing to the subject-matter, we must pronounce the work before us of exceeding value. Not only are the oils and fats very sparingly endowed with those striking properties which serve us in the diagnosis of metals, but they and their preparations have been seized upon by the greed of the present age, and falsified with a perseverance worthy of a better cause. Hence though their properties, physical and chemical, have been diligently scrutinised, cases still arise where the judicious analyst is not enabled to pronounce a decided opinion as to the presence or absence of fraudulent admixtures and substitutes,—"surrogates," as our German neighbours call them. Further, not a few oils and fats vary in their properties, according to the country where they have been produced, the conditions to which they have been subject, and the age of the sample.

Amongst the physical methods here described spectroscopical examination takes a place. An admixture of vegetable oils with those of animal origin may be detected by the absorption bands due to the presence of chlorophyll. "Olive and linseed oils give three absorption bands,—a very dark one in the red, a faint one in the orange, and a distinct one in the green." According to Daumer, the oils may be arranged spectroscopically in four classes:—

"1. Oils showing the spectrum of chlorophyll: olive oil, hemp-seed oil, and nut oil.

"2. Oils without any light-absorbing power: castor and almond oils.

"3. Oils absorbing the (so-called) chemical rays of the spectrum — the red, orange, yellow, and part of the green, remaining unabsorbed.

On examining such oils the spectrum from red to green remains quite normal, while the other parts are invisible. Here belong rape oil, linseed oil, and mustard-seed oil.

"4. Oils showing absorption bands in the different parts of the spectrum: sesame oil, arachis oil, poppy-seed oil, and cotton oils."

Concerning the value of the refractive power of different oils, authorities are not quite unanimous. The refractometers of Abbe and Zeiss are here figured and described, as also the oleo-refractometer of Amagat and Jean, based on an arbitrary scale.

The polariscope yields also results of some value, the instrument used being Laurent's saccharimeter, having a tube of 20 c.m. The microscopical appearance, the electric conductivity, and the determination of the specific gravity are also employed. The instrument preferred for this last determination is Stohmann's picnometer. Recourse has also been had to the melting- and solidifying-points.

But in all these tests, as well as in the chemical reactions, much trouble and frequent discrepancies arise from the great difficulty of obtaining for comparison samples of absolute purity. We suspect that analysts have sometimes been knowingly and intentionally supplied with sophisticated or abnormal specimens, in order to lead them and their colleagues into errors and bring the scientific examination of oils into mistrust and contempt. The pattern test first proposed by Tomlinson, and subsequently developed by Wynter Blyth, gave definite results only after a very prolonged series of experiments.

The chemical methods most used in the analysis of oils are the saponification value, the Reichert-Meissl value, the iodine and bromine values, and the acetyl value. The Maumené test—the rise of temperature observed on adding concentrated sulphuric acid—is rightly considered a valuable method for detecting sophistications, especially in the case of olive oil—the kind most liable to fraudulent admixtures,

Colour reactions, it is here pointed out, must be used with extreme caution, since small quantities of foreign substances, purposely or accidentally present, may give misleading indications.

The question of rancidity is ably treated. It is shown (Ballantyne and Heyerdahl) that free fatty acids alone do not occasion rancidity. Nor is this change due to the action of micro-organisms. Ritsert has shown that bacteria, whether aërobic or anaërobic, speedily die if introduced into fat. Rancidity seems due to the joint action of air and light. The larger the proportion of stearic and palmitic acids in a fat, the less is its liability to rancidity. The generally rancid condition of palm oil is doubtless due to the dirty manner in which it is collected by the natives.

We cannot prolong our notice of this interesting work. It will prove of the utmost value to all persons using oils and fats in the arts,—and they are a very numerous body,—as well as to analysts. Dr. Lewkowitsch has greatly enriched our technical literature by reproducing Prof. Benedikt's work in an English dress.

Organic Chemistry; the Fatty Compounds. By R. Lloyd Whiteley, F.I.C., F.C.S., Principal of Municipal Science School, West Bromwich. Crown 8vo., pp. 291. London and New York: Longmans, Green, and Co. 1895.

The author of this work confines himself to the so-called fatty compounds, which have lately enjoyed a smaller share of attention than the aromatic series.

After some useful introductory matter, touching chiefly on the sources and the purification of organic substance, he goes on to ultimate analysis of organic compounds, to the determination of percentage composition, and of molecular formulæ. Here we find an exposition of the determination of vapour density and of Raoult's cryoscopic method. Both these operations are necessary in research, and both are less generally known to chemists than would be desirable.

In speaking of the constitution of carbon compounds, Mr. Whiteley does not forget to caution his readers that the bonds have no actual existence, and are merely a convenient method of expression.

In the successive sections of the work the author discusses the fatty hydrocarbons, the haloid paraffins, the monohydric alcohols and their derivatives. The unfortunate fact is here mentioned—though without comment—that in Britain the official and commercial alcoholometric standard is not absolute, but "proof spirit." This is, we think, quite as unscientific as the retention of our traditional weights and measures.

In Section III. we have an account of cyanogen and its derivatives, substances which latterly, since the introduction of the coal-tar colours, have lost much of their technical importance.

In successive sections there follow the derivatives of the unsaturated hydrocarbons, of the dihydric and the polyhydric alcohols. It may edify certain orators to find that the name alcohol is no longer the exclusive property of the liquid against which they are contending, but a generic term.

The instructions given in this work, though necessarily concise, are clear and accurate, and the illustrations are exceedingly well drawn. There are here no lists of questions which have been set at examinations, nor references to any "syllabus," or any other of the characteristic features of the cram-system. Students who wish to *know* will find Mr. Whiteley's work a trustworthy guide.

Annual Report on the Year 1894. By E. Merck, Darmstadt. Published in March, 1895.

The very appearance of this work in the English language is a proof of the remarkable enterprise of its publisher. The Report consists of three parts. Of these, the first is composed of original communications; the second is devoted to pharmaceutical preparations; and the third to drugs.

Of these sections the second displays an admirable amount of research, which cannot fail to be of great value in medical practice, and to bear ultimate fruit in the treatment of disease.

The nomenclature is to some extent that recognised among German physicians and pharmacists; but certain features liable to puzzle an English reader, and leading him to mistake, *e.g.*, chloride for chlorate, have been avoided.

The weights and measures used are chiefly those recognised in England, and when the metric system is followed it is specially pointed out.

This pamphlet is, on the whole, written in very correct English. We may, however, point out that with us the symbol for iodine is I, not J.

List of Apparatus, &c., required for Teaching Practical Elementary and Advanced Physics, in accordance with the New Science and Art Regulations. Manufactured and Sold by Philip Harris and Co. (Ltd.) Edmund Street, Birmingham.

The list comprises elementary apparatus for a two years' course of experimental study. There are also sets of apparatus for the more advanced student in heat, sound, light, magnetism, and electricity. We are happy to notice that the optical apparatus includes a table spectroscope, the use of which instrument has been hitherto too much neglected in this country. The same must be admitted concerning the polariscope and saccharometer. We are bound to mention that the prices for the apparatus are exceedingly reasonable. No one can complain of having to pay, *e.g.*, £6 10s. for a table spectroscope properly fitted, or £3 10s. for a usable microscope.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 12, March 25, 1895.

New Researches by Prof. Ramsay on Argon and Helium.—M. Berthelot.—(See p. 176).

Remarks on the Spectra of Argon and of the Aurora Borealis.—M. Berthelot.—(See p. 176).

Researches on the Metals of Cerite.—P. Schützenberger.—This memoir will be inserted in full.

New Method of the Preparation of Chloroplatinous Acid and its Salts.—Leon Pigeon.—The author takes the reducing agent in weight equal to the theoretic quantity which should react. The chloroplatinic acid which is to be transformed is first weighed. The crystals which it produces when the solution is evaporated answer to the formula $PtCl_6H_2+6H_2O$. A mol. of this product (517 grms.) is exactly saturated by 1 mol. of barium carbonate, pure and dry (197 grms.), which is weighed out before allowing it to react. The liquid then contains exclusively barium chloroplatinate. He then weighs out a mol. of barium dithionate, crystalline, $S_2O_6Ba+2H_2O=333$ grms. This substance is dissolved in three times its weight of hot water. The two liquids are then mixed in a flask closed completely with a glass stopper. The flask is heated to 100° in the water-bath for twenty-four hours, when it is gradually modified, and takes the red colour of the chloroplatinites.

Action of Ortho-amino-benzoïc Acid upon Benzoquinone.—J. Ville and Ch. Astre.—Ortho-amino-benzoïc acid behaves with benzoquinone like the primary amines with simple functions. The formation of the product obtained from the acetic mother-liquors shows that benzoquinone presents certain properties common to the diacetones.

Variations of Saccharine Matters during the Germination of Barley.—P. Petit.—Saccharose increases continuously, but slowly, from the third to the sixth day. Diastase makes its appearance only on the fourth day.

Chemical Process for the Purification of Waters.—F. Boardas and Ch. Girard.—The authors use calcium permanganate, which removes organic matter and all micro-organisms. The reactions are:—Decomposition of the calcium permanganate in presence of organic matter with formation of calcium carbonate and manganese oxides; oxidation in the mass (composed of coke and manganese oxide) of the lower oxides of manganese at the expense of the excess of calcium peroxide; lastly, slow reduction of the manganese peroxide thus formed by the organic matters, or by the coke itself.

Formation of a Perfect Vacuum, even in Large Recipient, without any Mechanism.—M. de Laurier.—The receiver is filled with a gas, such as oxygen, capable of being absorbed by iron heated to redness.

Revue Universelle des Mines et de la Metallurgie. Vol. xxviii., No. 3.

Process for Enriching Phosphatic Limes.—P. Tarbary.—Hitherto the enrichment of calcareous phosphates has been aimed at by the removal of worthless matter. The calcium carbonate has been causticised by burning, and has then been dissolved away in water. The author proposes to use the phosphatic limes or basic slags in the iron manufacture, in place of common limestone.

Discovery of a Deposit of Calcium Phosphate in the Cretaceous Deposits of Brabant.—Prof. G. Lambert.—This deposit has been found in sinking an artesian well at Brussels. The proportion of phosphate has been found to be from 9 to 11 per cent, at depths of 108 to 122 metres.

Annual Production of Phosphates in the World.—

	Tons.
Belgium	450,000
France	450,000
England (coprolites)	20,000
Germany (coprolites and phosphorites)	50,000
Spain	50,000
Russia	75,000
Norway (apatites)	20,000
Algeria	7,000
Canada	20,000
North Carolina	7,500
South Carolina	600,000
Florida	500,000
Mexico (guano)	5,000
South America (guano)	60,000
Haiti	2,000
India	20,000

Consumption of Chemical Manures.—

	Tons.
Austria	100,000
Belgium	300,000
France	1,100,000
Germany	1,500,000
Holland	150,000
Italy	100,000
Norway and Sweden	100,000
Britain	1,100,000
Spain	100,000
United States	1,555,000

—*Le Phosphate.*

MISCELLANEOUS.

Electro-Chemistry in France.—The Société Industrielle of Rouen is offering a Gold Medal, among a number of others, for a new application of electro-dynamic machines to the chemical industry. All competitive essays, drawings, &c., are to reach the President of the Society by the 2nd September next.

The late Prof. von Helmholtz.—It is proposed to erect a statue in memory of the late Prof. von Helmholtz, and a Central Committee has just been formed in Berlin in connection with the matter. A Sub-Committee has also been appointed to convene meetings in various towns in connection with the movement, and also to organise in large local committees. Already a large number of subscriptions have been received.

Bismuth Nitrosalicylates.—H. Causse.—It results that even in a dilute solution nitric acid combined with bismuth oxide transforms salicylic acid into β-nitrosalicylic acid capable of yielding a series of salts the aspect of which varies with their composition. This property of nitrosalicylic acid seems to be due to the group NO_2 in its molecule. As in the other nitro-compounds, the phenolic function is heightened. Its aptitude for combination being thus rendered greater, explains the existence of a series of compounds previously obtained with salicylic acid. The presence of iron is not indispensable for the red colouration of bismuth salicylate.—*Bull. de la Soc. Chimique de Paris.*

MEETINGS FOR THE WEEK.

Wednesday, 17th.—Meteorological, 8.
—— Microscopical, 8.
Friday, 19th.—Quekett Club, 8.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1847.

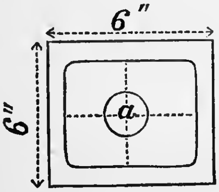
ON THE DIMINISHING OF PIPING IN CRUCIBLE-STEEL INGOTS CAST FOR TOOL MANUFACTURE.

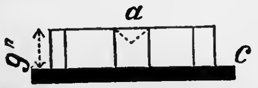
By SERGIUS KERN, M.E., St. Petersburg.

We think the following short notice will be of interest to metallurgists.

In order to avoid as much as possible the nuisance of piping in ingots, we propose the following method for casting crucible-steel used in the manufacture of various workshop tools, made by forging:—

The cast-iron moulds into which the charge of each crucible (⅝ of a cwt.) is poured into, are of the following design:—





The stand, *b*, is a block of cast-iron 3 inches thick; the lid is 2 inches thick (not shown). The mould is open from both ends, and is 2 inches thick. The dotted lines show the direction of the cutting of the steel ingots, previously heated, under the steam-hammer; the centre, *a*, is cut out, and is refuse (the pipe). The four blocks obtained are heated and drawn out into suitable bars.

SOLUBILITY AS A CLUE TO THE GENESIS OF THE ELEMENTS.

By C. T. BLANSHARD, M.A.

For the subject of solubility, in so far as it bears on the genesis of the chemical elements, the authorities that I have consulted are:—1. "Watts' Dict. Chem.," last ed.; 2. Storer, "First Outlines of a Dictionary of Solubilities," Cambridge, U.S., 1864; 3. R. Godeffroy, B.* 9, 1363 (coefficients of solubility of salts of the alkali metals).

Of the theories of solubility, so far propounded, *e.g.*, Berthelot and Jungfleisch (Bl. 13, 303), who regard solution as intermediate between simple mixture and chemical union; S. U. Pickering (B. 24, 3629), who explain solution as due to residual chemical affinity, the investigations of A. Belohoubek, of Prague (quoted shortly in C.C. 1880, p. 446); and of T. Carnelley (P.M. [5], 13, 180), are those which throw most light on the genesis of the elements. Belohoubek proves that of organic substances consisting of carbon and hydrogen, with or without oxygen—1. Substances free from oxygen are insoluble in water; 2. The richer a compound in oxygen, the more soluble it is in water; 3. Bodies dissolve each other better the more closely they resemble each other in structure.

Carnelley showed that of two or more isomeric bodies, that one dissolves most easily which has the lowest melting-point and in which the atomic arrangement is the least symmetrical.

Accurate data as to solubility at present to hand are the following, in which the solubility is reduced to uniform terms for the sake of comparison, namely the ratio of the weight of substance to the weight of water (that being the solvent considered as affording most data) required to dissolve it at a constant temperature, 15°.

Salt.	Solubility.	Salt.	Solubility.
$LiCl$	1 in 1·4 of water.	$LiBr$	1 in 0·6 of water.
$NaCl$	1 in 3·0 ,,	$NaBr$	1 in 1·3 ,,
KCl	1 in 2·8 ,,	KBr	1 in 1·5 ,,
$RbCl$	1 in 1·25 ,,	$RbBr$	1 in 1·0 ,,
$CsCl$	Very soluble.	$CsBr$	?
$LiNO_3$	1 in 1·5 of water.	Li_2SO_4	1 in 3 of water.
$NaNO_3$	1 in 1·4 ,,	$Na2SO_4$	1 in 7 ,,
KNO_3	1 in 5·0 ,,	K_2SO_4	1 in 10 ,,
$RbNO_3$	1 in 0·5 ,,	Rb_2SO_4	1 in 2·5 ,,
$CsNO_3$	1 in 8·0 ,,	Cs_2SO_4	1 in 0·5 ,,

With the exception of $CsNO_3$, the same regularity is observable as in the other groups of salts.

In the Zn group we have reliable data only in the case of the chlorides.

Salt.	Solubility.	Salt.	Solubility.
$ZnCl_2$	1 in 1·2 of water.	$ZnSO_4$	1 in 2 of water.
$CdCl_2$	1 in 3 ,,	$CdSO_4$	1 in 5? ,,
$HgCl_2$	1 in 14 ,,	$HgSO_4$	Decomposed by water.

Much more complete data are available for the alkali earths.

Salt.	Solubility.	Salt.	Solubility.
$BeCl_2$	Very sol. in water.	$Be(NO_3)_2$	1 in 0·5 of water
$MgCl_2$	,, ,, ,,	$Mg(NO_3)_2$	1 in 1·0 ,,
$CaCl_2$	1 in 0·25 of water.	$Ca(NO_3)_2$	1 in 3? ,,
$SrCl_2$	1 in 1·5? ,,	$Sr(NO_3)_2$	1 in 5 ,,
$BaCl2$	1 in 2·0 ,,	$Ba(NO_3)_2$	1 in 12 ,,
$BeSO_4$	1 in 1 ,,		
$MgSO_4$	1 in 3 ,,		
$CaSO_4$	1 in 360 ,,		
$SrSO_4$	1 in 7000 ,,		
$BaSO_4$	1 in ∞ ,,		

Only sporadic examples of solubility are to be had in the Si and P groups; therefore I shall not quote compounds of these. In the iron groups we have the following results:—

Salt.	Solubility.	Salt.	Solubility.
$FeCl_2$	1 in 2 of water.	$CoCl_2$	Slowly sol. in water.
$RuCl_2$	Insol. in ,,	$RhCl_2$	Insol. in water.
$OsCl2$	Sol. in small quantity of water, decomposed by large.	$IrCl_2$	,, ,,
$NiCl_2$	Very sol. in water.		
$PdCl_2$	Slightly sol. in ,,		
$PtCl_2$	Insol. in water.		

Chlorides of the halogens and chlorides and sulphates of the Al group furnish fairly comparable data.

Compound.	Solubility.	Compound.	Solubility.
BCl_3	Decom. by water.		
$AlCl_3$	1 in 1·4 of water.	$Al_2(SO_4)_3$	?
$ScCl_3$	?	$Sc_2(SO_4)_3$	?
YCl_3	Sol. in water.	$Y_2(SO_4)_3$	1 in 30 of water.
$LaCl_3$	Very sol. in water.	$La_2(SO_4)_3$	1 in 5 ,,
FCl	?		
$ClCl$	Rather sol. in water.		
$BrCl$	Sol. in water.		
ICl	Very sol. in water.		

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* Abbreviations as in "Watts' Dictionary."

We derive from the above figures, though in some cases they are rather meagre, together with Belohoubek's generalisations, the following laws of solubility:—

1. Bodies dissolve each other the more they resemble each other in structure.
2. In salts of groups II. and II.A. (*metallic* groups; for this division of the elements see P.M. [5], 39, 108) the solubility in water varies inversely as the atomic weight of the metal.
3. In salts of group I. (metallic elements) the solubility in water gradually decreases to the third member, potassium, and then increases until it reaches a second maximum with cæsium.
4. In salts of the intermediate and non-metallic groups (though here data are very defective), the solubility in water varies directly as the atomic weight of the metal, or electro-positive element.

Thus, according to law (1), simple compounds are soluble in water, more complex compounds in more complex liquids, as ether, alcohol, benzene, &c. This law, applied originally by its author to organic substances, admits of extension to all bodies, whether elements or compounds. Thus, many metals are soluble in hydrogen, as palladium. A still larger number are soluble in carbon, as Fe, Mn, Ni, Al. Metals also dissolve in each other, sometimes to an indefinite extent, but very generally to form alloys of definite constitution, able to crystallise. This is exactly analogous to salts crystallising with definite amounts of water.

Again, non-metals, which are, as a rule, insoluble in water, dissolve in various organic substances, as benzene, carbon disulphide, &c. Metals which dissolve in each other and in hydrogen, or the element carbon, are insoluble in such complex bodies.

It follows, therefore, that non-metals, from the point of view of solubility, are more complex, and therefore more highly evolved substances than metals. Sulphates, which are not of such simple structure as chlorides or bromides, or even as nitrates or chlorates, having more atoms in the molecule, are, as a rule, less soluble.

A good example of higher evolution, as indicated by increasing complexity of the solvent with increase of atomic weight of the non-metallic constituent, is to be found in the halogen salts of silver:—

AgF, soluble in water.
AgCl, very soluble in ammonia.
AgBr, soluble in ammonia.
AgI, nearly insoluble in ammonia.

Or, taking the actual figures for the solubility in ammonia only, we have, according to "Watts' Dictionary," reduced to a uniform standard as before—

AgF,	very soluble in	ammonia.
AgCl,	1 in 14 of	,,
AgBr,	1 in 20 of	,,
AgI,	1 in 2500 of	,,

New Volumetric Process for the Determination of Nickel.—F. Lecœuvre.—The process depends on the immediate precipitation of nickel by potassium cyanide in a solution feebly ammoniacal, and on its re-solution in an excess of the reagent. The solution of cyanide is at 10 per cent; each c.c. corresponds to 22 or 23 m.grms. of nickel. It is standardised with a solution of nickel and ammonia double sulphate. The commercial salt contains about 14·93 per cent of nickel. The author operates at the common temperature, adding to the neutralised solution a few c.c. of ammonia at 5 per cent. He runs in the cyanide by degrees, stirring constantly, until an additional drop transforms the turbid liquid into a transparent yellowish solution. The liquid must not be diluted. The presence of ammoniacal salts or of a small quantity of ammonia does not interfere.—*Revue Universelle des Mines et de la Metallurgie*, xxviii., No. 3.

RESEARCHES ON THE METALS OF CERITE.

By P. SCHÜTZENBERGER.

Notwithstanding numerous determinations the atomic weights of the metals of cerite do not seem to be established with all the certainty which might be desired. There is here no question of a precision of the order of that introduced by Stas in the determination of equivalents. The differences between the numbers proposed by various experimentalists bear most frequently upon the whole numbers, and sometimes reach several units.

Thus for cerium, the one whose oxide is easiest to separate in a high state of purity, the value of the atomic weight has varied from 137·1 to 142·3; the most recent determinations of Brauner (1885) and of Robinson (1884) approach closely to 140 (139·75 to 140·43).

It is evident that discrepancies so considerable cannot be ascribed to the degree of precision used in the analyses, but depend on causes of errors inherent in the methods employed. I have sought, by means of a series of experiments conducted methodically, to account for the nature of these disturbing causes, so as to avoid them. My attention has been specially directed to the analysis of cerium sulphate, a salt easy to obtain in a state of great purity, and in the form of fine crystals, by evaporating its aqueous solutions on the water-bath, taking advantage of its less solubility in hot than in cold water.

The excellent method due to an eminent and regretted colleague, Debray (fusion of the nitrates with eight or ten times their weight of saltpetre, between 320° and 330°), enables us easily and quickly to separate cerium in the state of dioxide from the didymium and lanthanum oxides, the nitrates of which are much more stable and only begin to decompose above 400°. If the operation is repeated two or three times, it yields a cerium oxide quite free from didymium and lanthanum. I indicate rapidly how I have obtained the pure cerium sulphate which has served for my experiments, following known methods except in some details:—

1. Treatment of the pulverised cerite with concentrated sulphuric acid.

2. Solution of the sulphates in pure water after expelling the excess of sulphuric acid; filtration; precipitation by hydrogen sulphide.

3. Evaporation of the liquid on a boiling water-bath in a capsule, an operation in which there separates rose-coloured crystalline crusts, formed of a mixture of cerium, didymium, and lanthanum sulphates.

4. The crystals separated from a ferruginous mother-liquor are dehydrated, re-dissolved in cold water, and the solution evaporated anew on the water-bath gave a purer deposit, which was re-dissolved; the solution is precipitated by ammonium oxalate. The mixture of oxalates, washed and dried, is dissolved in heat in an excess of pure nitric acid, and heated to the complete destruction of the oxalic acid. The solution of the nitrates is evaporated to dryness, the residue is mixed with 8 parts of saltpetre; the mixture is melted, and kept in fusion between 310° and 325° until the cessation of all escape of nitrous vapours.

5. The yellow cerium dioxide which separates is isolated by washing with hot water; the washing is completed with a solution of ammonium nitrate, to prevent the cerium dioxide from passing through the filters in a milky state. After ignition it is re-converted into sulphate, into oxalate, and lastly into nitrate, which is submitted to a second fusion with saltpetre at 320°. We thus eliminate the didymium which has been carried down on the first fusion, and we obtain a dioxide the solution of which no longer presents the absorption rays of the salts of didymium.

6. The white dioxide, faintly yellowish, thus obtained is transformed into cerium sulphate by concentrated sul-

phuric acid; the cerium sulphate is heated a little below an incipient dull red, and converted into cerous sulphate, $2[(SO_4)_2Ce]=(SO_4)_3Ce_2+SO_3+O$.

This last is dissolved in cold water, and the clear filtrate is evaporated on a boiling water-bath. The cerous sulphate is gradually separated during the evaporation in colourless prismatic crystals. When a large quantity has accumulated against the sides of the capsule, the mother-liquor is decanted off; the dehydrated crystals are re-dissolved in the cold, and the solution is separated in the water-bath, which furnishes a second crystallisation and a second mother-liquor. This new crystallisation is heated like the first. We continue thus, repeating the same series of operations five or six times. Finally, the last crystallisation may be regarded as sufficiently pure, and may serve for the analyses.

The crystals are crushed and dried in a boat through which is passed a current of dry air, whilst it is heated to 440° by means of the vapour of sulphur. All the water of crystallisation is thus expelled without separating the least trace of sulphuric acid. Under these conditions the salt loses 13·66 per cent of its weight, which corresponds to 5 mols. of water for an atomic weight of cerium bordering on 139·5. Without entering into the details of the numerous experiments effected in order to seek out the causes of errors inherent in the various methods which may be followed in the analysis of pure cerium sulphate, I will confine myself to indicating the conclusions at which I have arrived.

It is not possible to determine the sulphuric acid exactly by precipitating with barium chloride a boiling solution of cerium sulphate acidified with hydrochloric acid. However we may proceed—as has been already observed by Marignac—the barium sulphate carries down with it cerium oxide in the form of sulphate or chloride, or in both states simultaneously. In fact this barium sulphate, after being well washed and ignited, becomes yellow if it is moistened with concentrated sulphuric acid and ignited again. The weight of cerium thus carried down, if calculated as sulphate, may reach 2·2 per cent of the crude barium sulphate. The weight of the barium sulphate obtained, augmented by that of the cerium sulphate carried down, coresponds to a higher weight of barium sulphate not formed.

The carrying down of the cerous salt may be avoided by proceeding as follows:—

The solution of cerous sulphate is poured into an excess of a hot solution of pure caustic soda, obtained by dissolving sodium in water. The whole is kept for some time in ebullition. The precipitate of cerous oxide is washed with boiling water by decantation. The filtrates are collected, acidulated with hydrochloric acid, and precipitated in heat with a very slight excess of barium chloride. If formed under these conditions the barium sulphate subsides well, and never passes through the filters as it does if we use a decided excess of barium chloride.

If thus applied this method yields results which do not present between one experiment and another a satisfactory agreement, or the atomic weights thence deduced are generally too high, and vary between 140 and 141·5. The error is due to the circumstance that a small fraction of the sulphuric acid is retained by the precipitate of cerous oxide in spite of the intervention of an excess of hot caustic soda.

We succeed in overcoming this difficulty by dissolving the cerous hydrate, washed by decantation in hydrochloric acid, and re-precipitating in pure soda. During these washings the cerous hydrate absorbs a little oxygen, and is partly converted into ceric hydrate insoluble in dilute hydrochloric acid; but this fact, which is little marked, does not interfere with the success of the operation. The analysis, if thus conducted, gives 123·30 barium sulphate for 100·00 anhydrous cerous sulphate, which leads to the atomic weight 139·45 for cerium, a value probably not far remote from the truth.

Brauner's method (ignition of anhydrous cerium sulphate, and weighing the residual dioxide) seems to avoid every cause of error by reason of its great simplicity. The results furnished are nevertheless variable, and depend on the temperature at which the ignition of the sulphate is effected. At a cherry-redness we expel the totality of the sulphuric acid; the weight of the residual oxide (CeO_2) leads to an atomic weight included between 139·8 and 140. If, on the contrary, we heat for some time to a white redness, the oxide loses weight, and the atomic weight calculated is 139·8 to 138·8. This variation may be explained by admitting a slight loss of oxygen, which is the more probable as we have to do with a peroxide.

We arrive at analogous conclusions if we proceed by synthesis:—A known weight of cerium dioxide is converted into cerium sulphate by means of concentrated sulphuric acid. The cerium sulphate, if moderately ignited near—yet below—incipient dull redness, is converted into white anhydrous cerous sulphate. After weighing with exclusion of moisture, the salt is dissolved in water, and collected again to weigh it and take account in the calculation of the small quantity of dioxide not attacked.

With the dioxide very light and finely divided, of a light lemon-yellow colour, obtained by burning cerous oxide at a low temperature, the results lead to the atomic weight 143; the same oxide heated for some time to dull redness gives 140·5 to 141; lastly, after prolonged ignition to a bright redness, almost white, we obtain again the value Ce = 139·0, which is given by the ignition of the sulphate at this temperature.

Hence the methods founded on the transformation of the sulphate into dioxide, or inversely on the conversion of the dioxide, want a fixed basis. In both cases the numbers vary with the temperature, and we have the right to ask to what temperature of ignition does the true cerium dioxide correspond?

The following experiment proves that oxides richer in oxygen than the dioxide may be formed by mere oxidation in the air, and without the assistance of oxygenated water:—

Cerous oxide precipitated by pure soda, well washed with boiling water, collected on a filter, and then dried on the stove at 100°, dries up in the form of a yellow porous mass; this mass, if dried at 440° and then at dull redness, loses between the two temperatures 0·7 per cent of its weight, and a further 0·7 per cent between dull redness and a cherry-red. It is on account of these uncertainties concerning the true composition of the peroxide in question that we are led to give the preference to the atomic weight 139·5, deduced from the analysis of cerous sulphate in the moist way.

In the course of these researches we have observed the following facts:—

The cerium dioxide obtained by two or three successive fusions with saltpetre at 320°, being converted into cerous sulphate quite free from didymium and lanthanum, if we fractionate in successive portions the crystals during evaporation of the solution on the water-bath, we find a decrease of the atomic weight of cerium calculated from the weight of the residue of the ignition (at bright redness) of the sulphate, a residue calculated as dioxide.

The following series, taken among many others which have given similar results, shows it distinctly:—

Crystallisation No. 1 .. .. Ce = 139·4
" No. 2 .. .. Ce = 139·05
" No. 3 .. .. Ce = 138·06
" No. 4 .. .. Ce = 135·2.

This decrease shows plainly the presence of strange earths in the cerium dioxide obtained by Debray's method. We shall soon return to this interesting point.—*Comptes Rendus*, cxx., p. 668.

THE CAUSE OF LUMINOSITY IN THE FLAMES OF HYDROCARBON GASES.*

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

(Continued from p. 183).

A small glass combustion tube was well supported, and heated to the highest temperature attainable with one of Fletcher's big blowpipes, whilst pure acetylene was slowly flowing through it, the heating not being commenced until the tube was filled with the pure gas, all air being thoroughly rinsed out. As the temperature reached the softening point of the glass, the acetylene apparently burst into a lurid flame at the point where it entered the zone of heat, and clouds of carbon swept forward through the tube; but, although the carbon particles had to traverse an inch or more of tube more highly heated than the point of entering the hot zone, it was only at this latter point that the luminosity was developed, proving beyond doubt that it was the heat evolved by the decomposition, and not the external heating, which caused the carbon particles to emit light.

If it is the decomposition of the molecule of acetylene which develops the heat which is the cause of the incandescence of the carbon particles, then, if acetylene could be burnt without decomposition, a non luminous flame should be produced. It is conceivable that this might be done by so diluting the acetylene that it would require a much higher temperature to break it up.

It was Heumann who showed (*Liebig's Annalen*, clxxxiii., Part I., pp. 102—131) that hydrocarbon gases may burn with luminous flames, *i. e.*, with separation of carbon in the flame, or with non-luminous flames, *i. e.*, without any separation of carbon, and that the maintenance of a high temperature is an essential condition of luminosity; a flame, the temperature of which has been lowered by any means, being no longer able to bring about the required separation of carbon. He also points out (*Ibid.*) that "combustible matter, when diluted with indifferent gases, requires to be maintained at a higher temperature, in order that it may burn with a luminous flame, than when it is undiluted with such gases."

Dr. Percy Frankland, in his researches on the effect of diluents upon the illuminating value of hydrocarbons (*Chem. Soc. Journ.*, xlv., pp. 30 and 227), showed that ethylene, which was capable of developing a light of 68·5 candles power when burnt by itself, became non-luminous when diluted with about—

Hydrogen	90	per cent.
Carbon monoxide ..	80	,,
Carbon dioxide	60	,,
Nitrogen	87	,,

results which all show that excessive dilution by inert gases destroys luminosity.

In order to see if dilution had the same effect upon acetylene, experiments were made by diluting it with pure hydrogen. The gases were mixed over water, the proportion of acetylene actually present in the gas being determined by analysis at the burner, as, although the water in both holder and meter was, as far as possible, saturated with the gas, yet, as the analyses show, the precaution was an important one.

Composition of Mixture.				Illuminating Value of Mixture per 5 c.c. when burnt in 00 Bray.
Made in Holder.		At Burner.		
Hydrogen.	Acetylene.	Hydrogen.	Acetylene.	
90	10	90·5	9·5	Nil
80	20	81·5	18·5	1·8
70	30	65·5	34·5	14·0
50	50	43·5	56·5	87·0

Showing that dilution with between 80 and 90 per cent of hydrogen rendered the acetylene non-luminous when the mixture was burnt from a burner suitable for the higher values of gas.

In order to determine the point at which luminosity was destroyed when consuming the mixture in a burner suited to develope the light from a gas of low illuminating power, the experiment was repeated, using a 3-inch flame burning from the London argand, and also from a No. 4 Bray union jet, the latter being employed as it is difficult to determine the temperature in the argand flame.

Analysis of Mixture.		Illuminating Value per 5 cub. ft.	
Hydrogen.	Acetylene.	Argand.	No. 4 Bray.
92	8	Not measurable	
91	9	Not measurable	
88·5	14·5	4·1	1·7

So that luminosity would be destroyed in the argand by dilution with about 90 per cent hydrogen, and in the No. 4 Bray with about 88 per cent.

The next point to be determined was whether the destruction of luminosity in the diluted acetylene flame was in reality due to dilution, rendering it necessary to employ a higher temperature for the decomposition of the acetylene, or to other causes.

In order to do this, a tube made of specially infusible glass, 4 m.m. in diameter, was taken, and the Le Chatelier thermo-couple was fitted into it in the same way as before, used with the platinum tube, and all air having been rinsed out by a current of the mixture to be experimented with, the gas was allowed to pass at a steady rate of flow through the tube, the point at which the thermo-couple was situated being steadily heated by the Fletcher blowpipe, whilst the temperature recorded on the scale was noted the moment that incandescent liberation of carbon commenced.

Percentage Composition of Gas.		Temperature necessary to cause Deposition of Carbon with Luminosity.
Acetylene.	Hydrogen.	
100	0	780° C.
90	10	896
80	20	1000

It was found impossible to obtain a glass tube which would stand temperatures higher than this; but on plotting out the points so obtained, and which give a fairly straight line, it is seen that even if the increase in temperature only continues for increased dilution in the same ratio as shown in the experimental determinations, which is extremely unlikely, the reason of the destruction of luminosity in highly-diluted hydrocarbon gases is at once explained, as an increase of each 10 per cent in the dilution would necessitate an increase of 100° C. in the temperature of the flame, and with 90 per cent dilution a temperature of over 1700° C. would be required to bring about decomposition.

My reason for believing that it is highly improbable that when dilution is great it only requires the same increment in temperature to bring about decomposition as when the dilution is small is that in all the work I have done on the effect of diluents upon luminosity, and also in Prof. Percy Frankland's researches upon the same subject, dilution with hydrogen and carbon monoxide acts regularly, and decreases the value of the illuminant in a direct ratio down to about 50 per cent, whilst when the degree of solution exceeds 60 per cent a rapid falling away in the luminosity takes place, a fact which I think points clearly to a regular *pro rata* rise of temperature being needed for increase in dilution up to between 50 and 60 per cent. whilst higher degrees of dilution need a far greater rise of temperature in order to bring about decomposition.

Moreover, it would be manifestly incorrect to look upon the percentage of acetylene present in the gas issuing

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* A Paper read before the Royal Society.

from the burner as being any guide to the degree of dilution existing at the point at which luminosity commences. As the two small streams of gas issuing from the holes in the union jet meet and splay themselves out into the flat flame, they draw in with them a considerable proportion of air, the quantity being governed by the pressure of the gas at the burner.

This can be clearly seen by the fact that a high value gas which burns from a union jet burner of a given size with a smoky flame, under a gas pressure of half an inch of water, will burn with a bright, smokeless, and rigid flame of greatly increased illuminating value when the pressure is raised to 2 inches, whilst an ordinary coal-gas of 16-candle value must be burnt from a flat-flame burner at a pressure of about 0·75 inch if the best results are to be obtained, the increase in air drawn in, if the pressure rises to a much higher degree, diminishing the illuminating value.

Then, again, the area of non-luminous combustion in a mixture of gases like coal-gas means that some at least of the hydrocarbons are consumed before the required temperature for their decomposition is reached, whilst the products of combustion formed in the lower part of the flame are mixed with the flame gases, partly by diffusion and partly by being drawn into it by the upward rush.

When a simple hydrocarbon like ethylene or acetylene is burnt alone, the whole of the heat required to bring about the decomposition has to be generated by the combustion, without decomposition, of a considerable proportion of the hydrocarbon, and this means considerable dilution at the spot where the luminosity commences, so that at the top of a non-luminous zone of an acetylene flame there is only some 14 or 15 per cent of acetylene present, diluted with nitrogen, hydrogen, water vapour, and the oxides of carbon, whilst, with a mixture of 10 per cent acetylene and 90 per cent of hydrogen, in some cases little or no acetylene could be found at the top of the inner zone of the flame, it either having diffused with the hydrogen and been consumed, or polymerised to other compounds.

It is manifest that the luminosity of a flame will be governed, not by the percentage of acetylene in the gas, but at the point at which the temperature is sufficiently high to bring about decomposition.

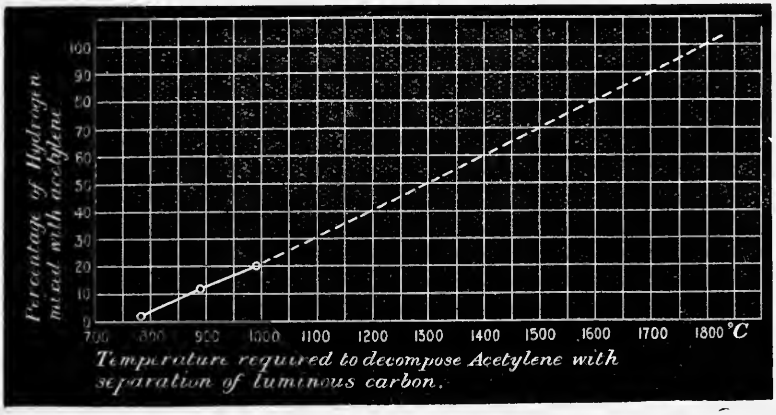

Fig. 1.

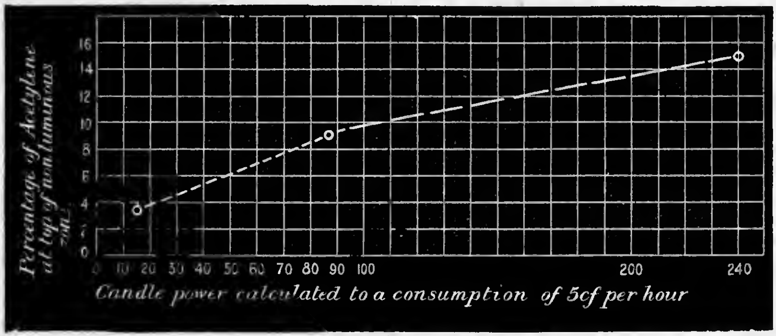

Fig. 2.

If, instead of making a mixture of 90 per cent hydrogen and 10 per cent acetylene, the hydrogen is burnt at the end of an open platinum tube, which has a fine platinum tube passing up the centre to the top of the inner zone of the flame, and if the acetylene be passed into the flame at the rate of one volume for every ten of the hydrogen, not only do we obtain an intensely luminous, but a very smoky flame.

In this experiment the gases were issuing from their respective tubes at the same pressure, but the small tube soon choked from deposited carbon, and it was found that the same results could be equally well attained by drawing down the inner tube to the level of the hydrogen tube, and making the acetylene issue at a slightly higher rate of flow, which hurried it in a compact stream through the inner zone of the hydrogen flame.

In order to see if the percentage of acetylene present at the top of the non-luminous zone bore any ratio to the illuminating value of the mixture, experiments were made in which mixtures of hydrogen and acetylene were burnt at a small flat-flame burner, and the percentage of acetylene was determined by gently aspirating out some of the flame gases from the top of the non-luminous zone.

Analysis of Mixture used.		Acetylene at top of Non-luminous Zone.	Illuminating Value of Flame for 5 cub. ft.
Hydrogen.	Acetylene.		
65·5	34·5	3·72	14·0
43·5	56·5	8·42	87·0
0·0	100·0	14·95	240·0

And on plotting out these results they certainly seem to point to the fact that, with flames of the same size burning from the same burner, the light emitted by the flame is directly proportional to the percentage of acetylene present at the top of the non-luminous zone of the flame, provided always that the temperature is sufficiently high to complete its decomposition.

(To be continued.)

SCIENTIFIC USES OF LIQUID AIR.[*]

By Professor DEWAR, M.A., LL.D., F.R.S.

When Faraday was working on liquid gases in this Institution about 1823, with such means as were then at his command, his inquiry was limited to the determination of specific gravities and vapour pressures of such bodies. Twenty years later, by the use of solid carbonic acid, the greatest cold then possible was obtained, and Faraday made admirable use of Thilorier's new cooling agent to extend his early investigations. Just as liquid carbonic acid produced in glass tubes was of no use as an agent for effecting the liquefaction of more resisting gaseous matters, until it could be manipulated in the solid state, so liquid air, until it could be handled, stored and used in open vessels, like any ordinary liquid, could not be said to possess scientific uses in any wide sense. Such operations become easy when double-walled vacuum vessels (such as were described in a former lecture) are employed in the conduct of experiments where substances boiling at very low temperatures have to be manipulated. The chief scientific use of liquid air consists in the facilities it gives for the study of the properties of matter at temperatures approaching the zero of absolute temperature. In this lecture the expression liquid air may mean either oxygen or air. Where a constant temperature is required oxygen is used. Liquid air made on the large scale may contain, after it is collected in open vacuum vessels, as much as 50 per cent of oxygen. Such a liquid boils between −192° and −182° C., and the longer it is stored the nearer it comes to −182° C., or the boiling-point of pure oxygen. For a number of experiments of a qualitative character, whether it is liquid air or oxygen that is used makes no difference. In many of the experiments to be recorded, liquid oxygen made from the evaporation of liquid air was employed. In pursuing this subject in consort with Professor Fleming,[†] a long series of experiments, involving the use of large supplies of liquid oxygen, have been carried out on the electric resistance of metals and alloys, and the results warrant the conclusion that at the zero of absolute temperature all the pure metals would be perfect conductors of electricity. Under such conditions a current of electricity started in a pure metallic circuit would develope no heat, and therefore undergo no dissipation. Similarly, we infer there would be no Peltier effect at the zero. In other words, the passage of electricity from one metal to another would take place without evolution or absorption of heat.

Further investigation, along with Professor Liveing,[*] on the refractive index of liquid nitrogen and air, has led to the conclusion that the refractive indices of nitrogen and air are respectively, for the D ray, 1·2053 and 1·2062. In these determinations, instead of using the prisms, we have employed the method of Terguem and Trannim, which consists in suspending in the liquid two plates of glass with a thin layer of air between them, and measuring the angle of incidence at which the chosen ray suffers total reflection at the surface of the air. As all the vacuum vessels are either spherical or cylindrical in form when filled with liquid, they act as lenses which are irregular and full of striations. Further, small bubbles of gas being given off in the liquid, rendered any image indistinct when viewed with a telescope. In order to avoid the necessity of observing any image through the liquid, it was used simply as a lens to concentrate the light observed on the slit of a spectroscope. Under such conditions the observations were easily executed and the results satisfactory.

For some time a series of observations on the thermal opacity of liquid oxygen and nitrogen have been projected. It is, however, exceedingly difficult to experiment in such a way as to eliminate the absorbing action of the glass vessels, and, as the use of rock salt is impracticable, the absorption of heat of low refrangibility remains for the present undetermined. It is possible, however, to use the glass vacuum vessels to determine approximately the relative thermal transparency for heat of high refrangibility, such as is radiated by a colza lamp. The following results represent the heat transmitted through the same vacuum vessels filled with different liquids, taking chloroform as the unit for comparison and correcting for differences of refractive index:—

Chloroform	1·0
Carbon bisulphide.. ..	1·6
Liquid oxygen	0·9
Liquid nitrous oxide ..	0·93
Liquid ethylene	0·60
Ether	0·50

From this result it follows that liquid oxygen is nearly as transparent to high temperature heat radiation as chloroform, which is one of the most transparent liquids next to carbon bisulphide. Liquid ethylene is much more opaque. These results must, however, be considered only as an approximation to the truth, and as generally confirmatory of the inferences Tyndall drew as to the relation between gases and liquids as absorbents of radiant heat.

Instead of silvering the interior and exterior of the vacuum vessels, it is found convenient when using mercury vacua to leave a little excess of liquid mercury, in order that the act of filling the inner vessel with liquid air should cause a fine silvery deposit of the metal over the exterior surface of the inner vessel. In such a vessel liquid air or oxygen shows no signs of ebullition, the surface remains as quiet and still as if it was ordinary water. The supply of heat is cut down to less than 4 per cent of what it is without exhaustion and silvering in good vacuum vessels. The result is that volatile liquids can be kept thirty times longer. Such vessels do not, however, maintain indefinitely the high standard of heat isolation they possess the first time they are used. After repeated use all vacuum vessels employed in the storage and manipulation of liquid air deteriorate. Illustrations of the appearance of such vessels are given in Figs. 1 and 2. The rapidity with which a space is saturated with mercury

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[*] A Lecture delivered at the Royal Institution, Jan. 19th, 1895.

[†] "The Electrical Resistance of Metals and Alloys at Temperatures Approaching the Absolute Zero." By James Dewar, LL.D., F.R.S., and J. A. Fleming, M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London. *Phil. Mag.*, 1892.

[*] "On the Refractive Indices of Liquid Nitrogen and Air." By Professors Liveing and Dewar. *Phil. Mag.*, 1893.

Fig. 1.

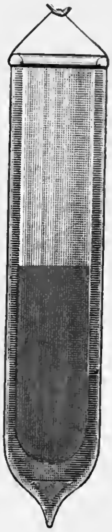

Fig. 2.

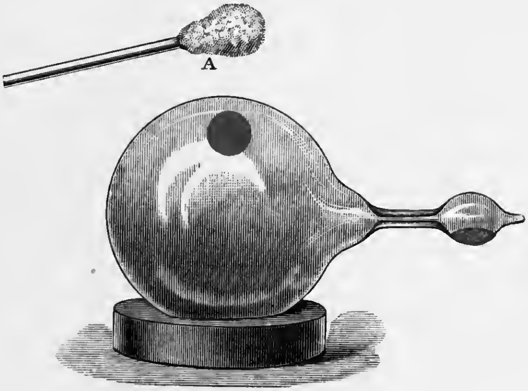

Fig. 3.

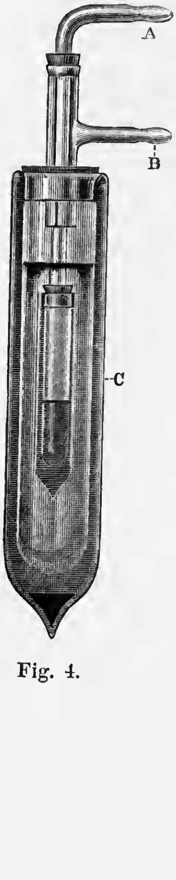

Fig. 4.

vapour (which we know exerts a pressure of about one-millionth of an atmosphere) is easily proved by simply filling a barometer in the usual way, and then instantly applying a sponge of liquid air to a portion of the glass surface of the Torricellian vacuum space, when a mercury mirror immediately deposits. It is important to know the amount of mercury deposited from a saturated atmosphere which is maintained (containing excess of liquid mercury) at the ordinary temperature, the condensation taking place when liquid air or oxygen is discharged into a vessel surrounded by such a Torricellian vacuum. If the deposit on the cooled bulb is allowed to take place for a given time, the outer vessel can then be broken and the amount of mercury which coated the bulb ascertained by weighing. Knowing the surface of the cooled bulb, the amount deposited per unit of area can be calculated. In this way it was found that in ten minutes 2 m.grms. of mercury per square c.m. of surface was deposited. Considering that one-tenth of a m.grm. of mercury in the form of saturated vapour at the ordinary temperature corresponds to the volume of 1 litre, this proves that the equivalent weight of 20 litres had been condensed in the space of ten minutes. This plan of cooling a portion of the surface of a vessel by the application of a liquid air sponge, enables us to test our conclusions as to the amount of matter present in certain vacua. Here is a globe of the capacity of 1 litre. It has been filled with, presumably, nothing but the vapour of mercury, by boiling under exhaustion and subsequent removal of all excess of liquid. Such a flask ought to contain mercury in the gaseous state that would weigh rather less than one-tenth of a m.grm., assuming the ordinary gaseous laws extend to pressures of less than one-millionth of an atmosphere. Now we know by electric deposition that one-tenth of a m.grm of gold can be made to cover one square c.m. of surface with a fine metallic deposit. Considering the general similarity in the properties of mercury and gold, we should therefore anticipate that if all the mercury vapour could be frozen out of the litre flask it would also form a mirror about one square c.m. in area. But after one such mirror is deposited, the renewed application of a second liquid air sponge to another portion of the surface would cause no visible deposit. This is exactly what takes place. If, however, two spheres, one much larger than the other, are joined together by means of a tube about 2 m.m. in diameter and 50 m.m. long, the whole space being a Torricellian vacuum (with some excess of mercury), then, on decanting, the mercury may be transferred to the smaller sphere, as is represented in Fig. 3. Now if an air sponge is applied to a portion of the surface of the larger sphere, a mercury mirror instantly deposits; but on applying a new air sponge to another portion of the surface, no further mercury mirror is formed. The narrow glass tube prevents the excess of liquid mercury in the small bulb supplying vapour rapidly to the larger one, so that the local cooling to – 180° C. of a portion of the surface has practically condensed all the mercury in the larger space, although the small one is still filled with saturated vapour and a free communication exists between them. If while in this condition the small bulb is inclined so as to allow a drop of liquid mercury to fall into the lower side of the large bulb, which has not been cooled, instant deposition of mercury takes place on the liquid air cooled portion of the upper surface. Under very small pressure of vapour, therefore, equalisation of pressure of two bulbs communicating by a narrow tube is a very slow process. There are cases, however, in which the application of a sponge of liquid air to the surface of a vessel causes no visible deposit, and yet the inference is that something has been condensed. The best arrangement to show this effect is to select highly exhausted vacuum tubes containing phosphorescent materials like alumina and other minerals, and to arrange the induction coil spark-gap of a little greater resistance than the vacuum tube. On starting the coil the current passes solely by the vacuum tube; but immediately the liquid air sponge cools a portion of the surface of the bulb, the discharge shifts to the air-gap. During the cooling the phosphorescence of the glass tube is greatly increased, but finally the resistance may become so great that all discharge in the vacuum tube ceases. Some old tubes belonging to the late Dr. De la Rue have given visible deposits near the electrodes, and in many the diameter and distribution of the striæ are materially changed during the local cooling to – 190° C. When large vessels containing nothing but mercury or iodine vapour as a residuum of the vacuum space are rubbed with a cotton-wool sponge of liquid air in a dark room, luminous glows filling the vessel take place occasionally, or bright flashes of light which enable the shape of the vessel to be seen. The ordinary mercury vacuum vessels show the same phenomena, which is doubtless due to electric discharges caused by friction and cooling.

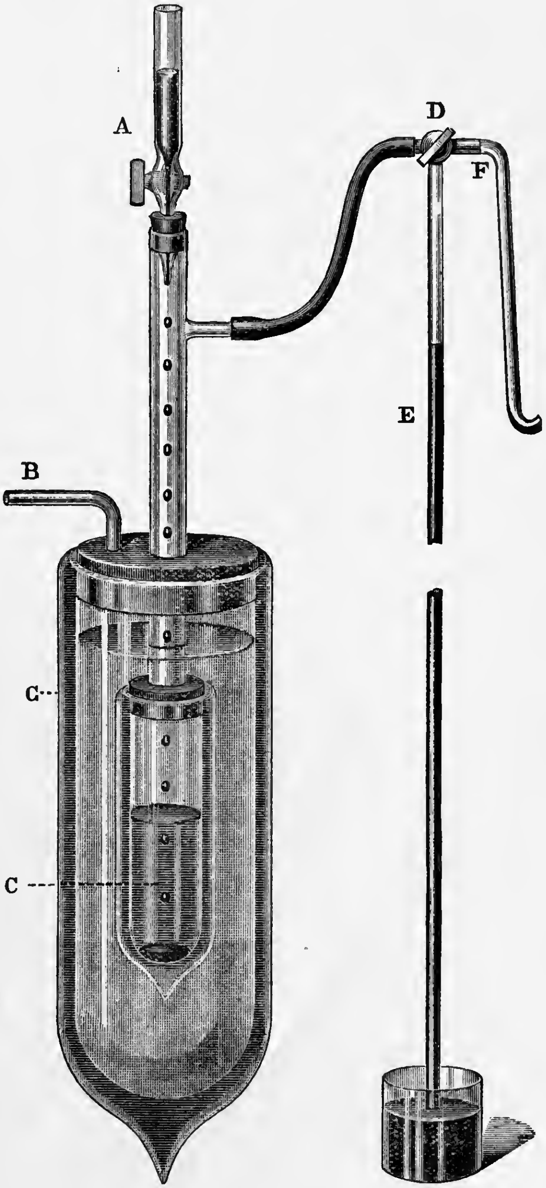

Fig. 5.

The optical properties of bodies cooled to the temperature of boiling liquid air will require long and patient investigation. An interesting fact easily observed is the marked change in colour of various bodies. Thus, for instance, oxide, sulphide, iodide of mercury, bichromate of potash, all become yellow or orange; while nitrate of uranium and the double chloride of platinum and ammonium become white. Chromic acid, dilute solution of iodine in alcohol, strong solutions of ferric chloride, and other coloured solutions, become greatly changed. Such facts are sufficient to prove that the specific absorption of many substances undergoes great changes at the temperature of − 190° C.

The tranquil atmosphere of air above the surface of the liquid in cylindrical or spherical vacuum vessels is a convenient place to cool very fragile bodies. During the slow ebullition of the fluid, gas between − 190° C. and − 180° C. is given off, which has three times the density of ordinary air, and which falls slowly over the mouth of the vessel in a heavy stream. On dipping into this atmosphere small soap bubbles, they contract rapidly and then freeze. If a soap film is made on a circle of thin wire about 2 inches in diameter, and allowed to stand until it shows the various orders of coloured bands, and is then carefully dipped into the cool air, it freezes, showing all the original colours. The black band is, however, always broken. Speaking of films, an interesting experiment may be made with a thin stretched sheet of india-rubber, such as is used for making balloons. It is well known that stretched india-rubber contracts when heated and expands when cooled. Now this can be shown very easily by covering a glass funnel or the end of a cylindrical vessel with a stretched sheet of rubber as thin as the walls of balloons. Such a surface is quite flat and fairly transparent. If a sponge of liquid air is drawn across the surface, the course is marked by a series of wrinkles, due to the temporary expansion of the rubber caused by the extreme cold. The sheet of rubber, being extremely thin, soon regains the ordinary temperature, and the surface then is as flat and tense as before. During the continuous motion of the cotton-wool liquid air sponge over the rubber surface, it is followed by wave-like depressions which disappear almost as quickly as they are formed. The elasticity of india-rubber, after cooling to − 182° C. and re-heating, seems unimpaired.

Organic substances that only become solid at very low temperatures may be divided into two classes—those which crystallise, and those which form glasses. Thus bisulphide of carbon, tetrachloride of carbon, methyl alcohol, hydride of amyl, all form crystals, whereas ethyl alcohol, amyl alcohol, turpentine, ethyl nitrate, chinoline, picolin, are glass-like. If a few drops of bisulphide of carbon are added to alcohol, and the mixture cooled to − 180° C., a white solid emulsion is formed, whereas the addition of tetrachloride of carbon to the alcohol resulted in the production of a clear solid without any separation. In the same way pure methyl alcohol crystallises easily, but the addition of a few drops of ethyl alcohol prevents crystallisation and causes a glass to be formed. Thus the examination of the behaviour of organic bodies at low temperatures may be a fruitful means of organic investigation.

For many purposes of investigation it is necessary to keep liquid air without evaporation. This is readily done by the use of two vacuum test-tubes, fitting freely one inside the other, arranged as in Fig. 4. The smaller one is filled with liquid air, and, after the insertion of an india-rubber stopper and glass tube, is completely immersed in liquid air contained in the larger vacuum vessel. In the figure the tube A connects with the inner vacuum tube, and B with the outer. As the latter receives all the radiant and conducted heat, air is continuously boiling off through the tube B; but as the supply of heat is effectually cut off from the inner vacuum vessel, also containing liquid air, no air distils through tube A. This is the most convenient arrangement to use for the production of solid air. For this purpose B is connected with an air-pump until the pressure is reduced to about ½ inch, and therefore the temperature about − 200° C. Then a good air-pump is put on to the inner vessel of liquid air (containing oxygen and nitrogen in the normal proportion of oxygen and nitrogen), by means of the tube A, while maintaining constantly the exhaustion in the outer vessel. In a short time the air in the inner vessel solidifies to a transparent jelly-like mass.

The same principle is used when the latent and specific heats have to be determined. Fig. 5 shows the general plan of the apparatus. Now a definite quantity of heat has to be conveyed into the inner vacuum vessel containing liquid air, with the object of finding the weight of liquid that distils off, on the one hand, or the elevation of temperature in the liquid that takes place on the other. For the purpose of adding a given quantity of heat it is convenient in some cases to use mercury (as represented in the figure), or to lower a piece of platinum or silver, or even glass, into the inner vessel: each unit of heat supplied evaporates a definite amount of air, which is readily ascertained by collecting the gas which comes off during the heat conveyance. In Fig. 5, A is the mercury, C the inner vessel of liquid air, D a three-way stopcock, F a tube for collecting the air given off; E is a barometric tube for observing the pressure when the inner vessel is exhausted. In a latent heat determination all that is necessary is to weigh the mercury added and to measure the amount of air by volume which has distilled from the liquid state. If the specific heat of the liquid is wanted, then the inner vessel is exhausted (as well as the outer) through the tube F to about ½ inch pressure, and the three-way stopcock turned so as to shut off F and connect the inner vessel with the manometer E. Mercury is now dropped into the inner vessel until the manometer rises to the atmospheric pressure or the liquid reaches its boiling-point under atmospheric pressure. Care must be taken to prevent the drops of mercury falling exactly in the same place, otherwise a mercury stalagmite grows up rapidly through the liquid, vitiating the results. Another objection to the use of mercury arises from the drops causing the rebound of small liquid air drops, which strike the cork and get evaporated away from the main body of liquid. The amount of mercury added conveys the necessary amount of heat needed to raise the given amount of liquid from its boiling-point under ½ inch pressure to its boiling-point under 30 inches. The relative pressures give the temperature range, and the weight of liquid air or other gas under observation is easily ascertained, together with the weight of mercury added. In this way the latent heat of liquid oxygen at its boiling-point is about 80 units, and the mean specific heat between − 198° and − 182° is 0·39

(To be continued).

ON THE
DETERMINATION OF TANNIC COMPOUNDS.

By AIMÉ GIRARD.

In 1882 (*Comptes Rendus*, xcv. p. 185) I published a process for the determination of the tannic compounds, which depends on the fixation of these compounds by an animal membrane of a definite and constant composition. This membrane consists of the intermediate coating of the intestine of the sheep,—a coating formed of pure muscular tissue, and which I obtained at first from the harmonic strings supplied in trade to musicians under the name of *violin ré.* This process has been repeatedly applied by various chemists, to whom it has yielded excellent results, whilst in the hands of others it has proved absolutely unsuccessful.

By occasion of a prolonged study of the composition of the grapes of the principal kinds of vines in France, undertaken two years ago by M. Lindet and myself,—the results of which we shall soon present to the Academy,—it has seemed necessary to resume the study of this procedure, and to search what can be the cause of success of some and the failure of others. I soon perceived that the cause must be sought in the unequal quality of the harmonic strings obtained in trade by the experimentalists.

At the time when I devised the process in question, M. Thibouville-Lamy kindly proposed for my purpose products of an exceptional purity. The chemists who have made use of my process have not always obtained specimens of a similar purity.

The intestines of sheep intended for the manufacture of fiddle-strings must be at first very carefully scraped on a die, to detach, on the one hand, the serous or peritoneal membrane, and, on the other, the mucous membrane, so as to lay bare the intermediate membrane formed exclusively of muscular fibres adhering together. It is then plunged into a solution of potassa, and treated sometimes with different reagents, and after being mechanically purified as just described, it is thus freed from fatty matter as completely as possible. At the same time it acquires such adhesive properties that if twisted with two or three similar membranes — spun, as it is technically called — it dries in the form of a solid cord, which constitutes a fiddle-string.

But without very special precautions, such as those adopted by M. Thibouville-Lamy, it is impossible to obtain under these conditions an animal membrane absolutely pure.

On examining with the microscope samples of the ordinary manufacture, even products already treated with care, I found that, adhering to the muscular tissue, there always remained some spots of the fatty tissue, whilst on the other hand the membranes, from the fact of their more or less prolonged maceration in an alkaline bath, in spite of repeated washings, retained always an important proportion of potassium carbonate and sulphate.

A number of specimens very carefully prepared gave the following results:—

	I.	II.	III.	IV.
Moisture	13·42	12·07	6·93	7·53
Fats	2·88	1·60	1·91	0·99
Soluble salts	10·56	10·46	5·01	6·10
Dry animal tissues ..	73·14	75·87	86·15	85·30

It is easy to understand that products thus loaded with impurities must in practice give bad results. The chemist must always present to the tanniferous liquid a known weight of animal tissue. But this tissue, if as impure as the foregoing samples, will give off to the water from 5 to 10 per cent of soluble salts; when tanned and dried at 100° to 105° it will lose 1 to 2 per cent of the fatty matter in the state of vapour; so that, in spite of the fixation of the tannin, its weight at the end of the analysis may be found less than the initial weight.

To avoid these errors it is sufficient to obtain strings carefully prepared in the ordinary manner, and complete their purification in the laboratory.

These membranes do not require to have been twisted in the form of fiddle-strings. It simply dried, and treated with sulphurous acid to ensure their preservation, will be fully sufficient for the determination of the tannic compounds.

The strings are then cut into threads of 0·15 metre in length, and submitted in the cold to the action of crystallisable benzene. These washings are repeated until the benzene no longer takes anything up. They are then exposed in the cold to the open air, and when the benzene has evaporated there follow three or four washings with cold distilled water.

When taken out of the water they are dried in cold air, moving them so that they may not cling together. They are then ready for use. All the causes of error are thus removed, and they may be safely used for the determination of the tannic compounds, according to the method described in 1882.—*Comptes Rendus*, cxx., 358.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1895.

Dr. Armstrong, President, in the Chair.

Messrs. George Thudichum and Arthur H. Coote were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harold Allden Anden, B.Sc., 102, Acomb Street, Manchester; Lancelot Alexander Borradaile, B.A., Selwyn Coll., Cambridge; Henry Bradford, 21, Kensington Mansions, Earl's Court, S.W.; Irving Foster Hasslewood, The Elms, Aulaby Road, Hull; Robert Charles Marchant, 18, Westfield Park, Redland, Bristol; Henry F. A. Wigley, B.A., 64, Quentin Road, Lee, S.E.

Of the following papers those marked * were read:—

*32. "*The Volumetric Determination of Sugars by an Ammoniacal Cupric Solution.*" By Zdenek Peske. (Communicated by Professor Brauner).

Being dissatisfied with Fehling's method and its rather lengthy modification by Allen, and with the gravimetric method of Soxhlet-Allihn, the author tried to find a rapid and reliable process of estimating sugar based on Pavy's method of working in an ammoniacal solution. The latter method fails on account of the rapidity with which the reduced ammoniacal cupric solution is oxidised by the air. The author avoids this by covering the solution with a layer of paraffin oil of high boiling-point ("white vaseline oil"). It is necessary to keep the amount of ammonia constant. The use of a current of indifferent gas was proposed to the author and tried by him some one and a half years ago, but was given up as the liquid rapidly loses ammonia, and its reducing factor is thereby so altered that constant results cannot be obtained. Tables are given showing the reducing power of a standard ammoniacal cupric solution (in presence of Rochelle salt) for liquids containing different amounts of (1) glucose, (2) invert sugar, (3) invert sugar in presence of cane sugar.

*33. "*The Action of Hydrogen Sulphide on Antimonic Acid Solutions.*" By Otto Bosek, Ph.D. (Communicated by Professor Brauner).

Berzelius, Rose, Rammelsberg, Bunsen, Willm, Thiele, and others, having obtained contradictory results, the question has been re-investigated.

The complete conversion of antimonious into antimonic compounds by the action of oxidising agents is difficult. Such agents as fuming nitric acid, potassium chlorate, and hydrochloric acid, and even bromine in alkaline solution, do not produce complete oxidation unless they act for a long time and are used in very large excess.

The experiments show the independent existence of compounds of the type SbX_4 (corresponding to the "antimonious acid" of Berzelius). The author has succeeded in obtaining a crystalline double salt of the tetrachloride $3KCl \cdot 2SbCl_4$, and also the pure tetrasulphide Sb_2S_4, differing from either the trisulphide or the pentasulphide in its crystalline form and its highly characteristic pink colour.

An excess of an aqueous solution of hydrogen sulphide acting on antimonic acid solution at ordinary temperatures forms antimony pentasulphide, thus showing that exact results are obtained when Bunsen's directions are strictly followed.

When hydrogen sulphide acts on antimonic acid solutions, the quantity of antimony pentasulphide increases (*a*) the lower the temperature, (*b*) the more rapid the stream of hydrogen sulphide; while the quantity of antimony trisulphide mixed with sulphur increases (*a*) the the higher the temperature, (*b*) the slower the action of the hydrogen sulphide. The quantity of the pentasulphide formed increases up to a certain limit (10 to 20 per cent) with the amount of hydrochloric acid present, after which it diminishes. Antimonic solutions are more easily and completely reduced by hydrogen sulphide in presence of a chromic salt.

*34. "*Action of Hydrogen Sulphide on Antimonic, Arsenic, and Telluric Acids.*" By B. Brauner, Ph.D.

When antimonic acid and hydrogen sulphide interact, one or both of the changes represented by the following equations may take place—

$$(1)\ H_3SbO_4+5H_2S=Sb_2S_5+8H_2O,$$
$$(2)\ 2H_3SbO_4+5H_2S=Sb_2S_3+S_2+8H_2O.$$

At first a solution is formed which apparently contains a colloidal modification of the pentasulphide, possibly H_3SbS_4. When antimonic acid is heated with hydrogen sulphide in a solution containing much free hydrochloric or sulphuric acid, antimony pentasulphide is precipitated. Neither oxysulphantimonic acid nor any oxysulphantimonate corresponding with the analogous arsenic compounds could be obtained.

The more positive behaviour of antimony, as compared with arsenic, is in accordance with the relative positions of these elements in the periodic table.

In its behaviour towards hydrogen sulphide, telluric acid resembles arsenic acid more than antimonic acid, but no oxysulphotelluric acid could be isolated. It is known that antimony pentasulphide is decomposed into the trisulphide and sulphur when heated to 220°. The author finds that the same change occurs when the pentasulphide is exposed to sunlight, and when it is heated with water to 98°, the trisulphide separating in the black crystalline form.

*35. "*The Atomic Weight of Tellurium.*" By Bohuslav Brauner, Ph.D.

In continuation of his work on the determination of the atomic weight of tellurium, published in the *Transactions*, 1889, p. 382, the author has re-calculated the numerical data then obtained, and on reducing to a vacuum finds the number 127·71, which is higher by 0·86 than the atomic weight of iodine 126·85, whereas from its position in the periodic system tellurium should have an atomic weight between 123 and 125. On this account he is led to the conclusion that tellurium is not a simple substance, a conclusion which is supported by the following considerations:—1. Tellurium precipitated and dried in a current of an inert gas gives higher values for the atomic weight than when sublimed in hydrogen. 2. The properties and composition of the dibromide. 3. The varying results obtained on attempting the synthesis of the dioxide, the basic sulphate, and certain metallic tellurides. 4. The behaviour of tellurous and telluric acid solutions towards hydrogen sulphide.

A large quantity of tellurium was therefore carefully purified by the process described in the paper referred to above, and, after being converted into sodium sulphotellurate, was submitted to a process of fractional precipitation similar to that used for separating the rare earths from one another. On examining these fractions it was found that there were variations in the equivalent of the tellurium dioxide as determined by the permanganate method described in the *Transactions*, 1891, p. 238. This variation, however, was found to be caused by the presence of minute quantities of mercury, thallium, bismuth, copper, and lead in the extreme positive fractions, and of arsenic and antimony in the negative fractions. On the other hand, the tellurium obtained by further purifying the middle fractions showed scarcely any variation in molecular weight.

In the course of experiments on telluric acid, made with the object of controlling the determination of the atomic weight of tellurium, the author has found that it is very difficult to prepare the acid in a pure state; moreover, it behaves like a mixture of two substances. He has also discovered a new modification of telluric acid corresponding with the yellow tellurates, the existence of which was predicted by Berzelius.

The discovery of argon inclines the author to believe that it is one of a new group of elements (or a mixture of them) in the periodic system—the Argon Group—coming between the last two groups, and if it be assumed that tellurium is a mixture, or alloy, or compound of the true tellurium with Argon No. 4, or "Triargon," it would consist of equal parts (atoms) of the two,—

$$\frac{125{\cdot}4 + 130}{2} = 127{\cdot}7,$$

and have the formula $Te_2A^4{}_2$.

*36. "*The Hydrolysis of Maltose by Yeast.*" By G. Harris Morris, Ph.D.

Until E. Fischer recently described (*Ber.*, 1894, 2985, 3479) experiments on the hydrolysing action of yeast on maltose, the opinion had been generally held that maltose is directly fermented by yeast, or that if hydrolysis take place, this phenomenon and that of fermentation occurred simultaneously, as it had never been possible to detect products of hydrolysis in a solution of maltose undergoing fermentation. Fischer has, however, shown that air-dried yeast and its extract, when digested with a solution of maltose, readily converts a very considerable proportion into dextrose, and also that the extract of moist yeast cells which had been ruptured by trituration with powdered glass possessed the same power. Moreover, in the second paper, he states that when unruptured yeast cells are digested with maltose solution for three days in presence of chloroform, some 40 per cent of that sugar is converted into dextrose. Fischer chiefly used pure cultures of Frohburg yeast in his experiments, but he also examined low-fermentation yeast, and pure cultures of other races, with similar results.

Having in view the important nature of the subject, and the bearing it has upon the determination of cane sugar in the presence of maltose by inversion with yeast, the author has repeated Fischer's experiments. He has obtained results confirming Fischer's statements as to the action of air-dried yeast and its extract, and also of ruptured moist yeast, but was quite unable to obtain any evidence of hydrolysis when moist and well-drained yeast was employed, although both pure cultures of Frohberg yeast and ordinary London brewery yeast were used. The experiments were made by digesting a 5 per cent solution of maltose with yeast (drained on a porous tile) in the proportion of 1 grm. of yeast to 100 c.c. of solution. The digestions were carried on for periods varying from twenty-four hours to three days at 35° C. in the presence of chloroform. The solutions were examined before and after the digestion, and dextrose was also tested for after digestion with phenylhydrazin acetate in the usual way. In all cases the optical and cupric reducing powers remained unaltered after digestion, and no trace of dextrose could de detected by the phenylhydrazin test. In order to further examine the question, maltose solutions were set to ferment, portions of the fermented liquid being withdrawn from time to time, and the matter remaining unfermented examined by the above tests. In no case was the slightest evidence obtained of the presence of dextrose, the analytical results showing the presence of maltose, and maltose only, in the fermenting solution.

In order to obtain some explanation of this remarkable difference in the behaviour of well drained but moist yeast, and of air dried yeast, a quantity of the former was digested with chloroform water for twenty hours, in order to kill the cells and then air-dried; any decomposition during drying, due to vital changes, was thus prevented. The dried yeast thus obtained possessed the same power as that dried in the ordinary way, and the author stated that Mr. F. W. Tompson had informed him that the yeast liquor, obtained as described in the paper of O'Sullivan and Tompson on invertase, which is manifestly a product of the decomposition of the yeast, and which possesses the power of inverting cane sugar to a most marked extent, was without action on maltose. That the action of dry yeast is not due to the cells being ruptured during powdering was shown by the fact that the horny mass remaining when yeast is dried on a porous tile was just as active when used in that form as when finely powdered before addition to the maltose solution.

The dry yeast has also the power of liquefying starch paste, and of producing dextrose from a starch-conversion from which all the soluble portions has been removed by repeated treatment with 80 per cent alcohol.

The author is making further experiments to ascertain the cause of the hydrolysing action of dry yeast.

37. "*Studies in Isomeric Change.* Part IV. *Ethylbenzene Sulphonic Acids.*" By Gerald T. Moody, D.Sc.

In previous communications (*Proc. Chem. Soc.*, 1888, 77; 1892, 90, 213, 214) the author has called attention to the ease with which certain orthosulphonic acids of benzene derivatives undergo isomeric change, and are thereby converted into parasulphonic acids. The investigation has now been extended to the ethylbenzenesulphonic acids. The ethylbenzene available for these experiments was obtained from Kahlbaum, and was evidently impure, as, when shaken with sulphuric acid, it gave a bright red colouration, not due to free iodine.

As it has been stated by Chrustschow (*Ber.*, vii., 1166) that ethylbenzene on sulphonation gives rise to two distinct acids, it was considered desirable to sulphonate a highly purified specimen of the hydrocarbon. To obtain such, the crude product of sulphonation of Kahlbaum's ethylbenzene was converted into barium salt, which was several times re-crystallised and then converted into sodium salt. The latter was repeatedly re-crystallised until no doubt as to its purity could exist, and then hydrolysed. The hydrocarbon thus obtained, which boiled at 135°, was sulphonated both with chlorosulphonic acid and with sulphuric acid. With each of these sulphonating agents one, and only one, sulphonic acid, namely, ethylbenzeneparasulphonic acid, was obtained. This behaviour of ethylbenzene is remarkable when compared with that of methylbenzene, which is known to give rise to a large proportion of ortho-acid on sulphonation. Ethylbenzeneparasulphonic acid forms a well-characterised barium salt which is anhydrous and does not contain 1 mol. of water of crystallisation, as stated by Sempotowski (*Ber.*, xxii., 2662), and a sodium salt which crystallises with ½ a molecular proportion of water. The sulphonic chloride solidifies in a freezing mixture and melts at 12°; the sulphonamide crystallises from water in needles, from alcohol in six-sided plates, and melts at 110°.

In order to obtain ethylbenzeneorthosulphonic acid, ethylbenzene was brominated and the resulting bromoethylbenzene sulphonated and coverted into barium salt. The less soluble barium salt which crystallises in characteristic, long, shining plates, is a derivative of parabromethylbenzeneorthosulphonic acid. It contains 3 mols. of water of crystallisation, and yields a beautiful sodium salt. The latter, on reduction with zinc-dust and sodium hydroxide, yields sodium ethylbenzeneorthosulphonic acid, which crystallises with 1 mol. of water. The orthosulphonic chloride is an oil; the orthosulphonamide melts at 97°. The acid obtained on heating the sulphonic chloride with water at 140° crystallises in white, deliquescent prisms. When it is heated at 100°, either in a tube through which a current of dry air passes, or in an open dish, it is rapidly converted into the para-acid. This change is unaccompanied by the liberation of more than a mere trace of sulphuric acid.

(To be continued).

Some New Combinations of Hexamethyleneamine.—M. Delépine.—The author describes the two chloromercurates, the double mercurate of hexamethyleneamine and ammonium, the iodo-mercurate, and the action of the phenylhydrazine hydrochlorate.—*C. R.*, cxx., No. 13.

NOTICES OF BOOKS.

On the Influence of Copper on Cast-Iron, Iron, and Steel. By V. Lipin, Mining Engineer, Chief Metallurgist of the Poutiloff Works. 69 pages (in Russian). St. Petersburg. 1895.

Under this heading M. Lipin has published a very interesting investigation. The objection to copper in iron and steel works, as is known, is exceedingly great.

By many careful experiments, elaborately conducted by M. Lipin at the extensive Poutiloff Works, the investigator has come to the definite conclusion that, though it is certainly not desirable for iron or steel to contain noxious elements, yet the presence of copper may be safely tolerated up to 0·5 per cent in wrought-iron and up to 1—2 per cent in cast-steel. Such metals behave in the same manner as material free from copper.

M. Lipin also reasonably remarks that many rich iron-ores, now lying idle only on account of containing 0·475 per cent of copper, in an oxidated form, could be safely used for the manufacture of cast-iron.

OBITUARY.

PROFESSOR LOTHAR von MEYER.

We regret to have to announce the death of Lothar von Meyer, Professor of Chemistry at the University of Tubingen, at the age of sixty-five. His decease is a considerable loss to science. He chiefly devoted his attention to the study of physiological and theoretical chemistry, and in both branches he contributed to an increased knowledge of the subject. His most important work, in which he developed his views on chemistry in general, is entitled "The Modern Theories of Chemistry."

PROFESSOR DANA.

Professor James Dwight Dana, the eminent mineralogist and geologist, died on the 15th inst. of heart failure. He had been Professor of Natural History and Geology at Yale College since 1855, and was a Fellow of the Royal Society of London, as well as member of the French Academy and of other scientific bodies in Europe.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 13, April 1, 1895.

Composition of the Water of Field Drains.—P. P. Dehérain.—The nitrogen which the crop does not take up in a bad season is carried off in the drainage. The losses from bare lands are infinitely greater than those from lands under crops. Hence the soil should be covered with vegetation as long as possible.

Prof. Ramsay, who was present at the sitting, gave verbally some account of the results which he has recently forwarded to the Academy, and which have already been inserted.

On a Radiometer of a Symmetrical Construction, Rotating by the Action of a Dissymmetric Illumination.—G. Seguy.—We have here a case of re-discovery, such a radiometer having been described by Mr. Crookes as far back as 1876.

Thermic Study of the Anhydrous Barium and Strontium Iodides.—M. Tassilly.—Formation-heat of solid BaI_2, setting out from its elements (x representing the oxidation-heat of barium:—Ba solid + I_2 gaseous = $x+13{\cdot}7$ cal.; Ba solid + I_2 solid $x+2{\cdot}9$ cal. Formation-heat of solid SrI_2 setting out from its elements:—Sr solid $+I_2$ gaseous$+123{\cdot}1$ cal.; Sr solid$+I_2$ solid$+112{\cdot}3$ cal.

Properties of the Nickel and Cobalt Salts.—M. de Koninck.—A reclamation of priority concerning the properties of the nickel and cobalt sulphides.

Calcium and Barium Alcoholates.—M. de Forcrand.—A thermo-chemical paper not adapted for useful abstraction.

Ammoniated Bases derived from Hexamethyltriamidotriphenylmethane and their Action on the Rosanilines.—A. Rosenstiehl.—According as a phenylic carbinol is amidated or ammoniated (in para) the alcoholic function is modified. In the amidated substances the alcoholic function comes first into play. In the ammoniated substances, on the contrary, the ammonium function is the first to act, and the alcoholic hydroxyl no longer reacts with the acids, but still reacts with the alcohols to form mixed ethers. When the same mol. contains nitrogen in two states of saturation, the function of the ammoniated base predominates still over the aminic and the alcoholic function. But there is a moment of hesitation between the two latter. The aminic function comes into play before the alcoholic function, though only in a transitory manner, and when an equilibrium is established by time, or by the intervention of heat, the alcoholic function still predominates over that of the double amine.

MEETINGS FOR THE WEEK.

Monday, 22nd.—Society of Arts, 8. (Cantor Lectures). "Recent American Methods and Appliances employed in the Metallurgy of Copper, Lead, Gold, and Silver," by James Douglas.
— Medical, 8.30.
Tuesday, 23rd.—Royal Institution, 3. "Alternating and Interrupted Electric Currents," by Professor George Forbes, F.R.S.
— Society of Arts, 8. "Art of Casting Bronze in Japan," by William Gowland.
— Institute of Civil Engineera, 8.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
Wednesday, 24th.—Society of Arts, 8. "The Use of Electricity for Cooking and Heating," by R. E. Crompton, Pres. Inst. Elect. Eng.
— British Astronomical Association, 5.
— Geological, 8.
Thursday, 25th.—Royal, 4 30.
— Society of Arts, 4.30. "The Coming Railways of India, and their Prospects," by J. W. Parry, A.M.Inst.C.E.
— Royal Institution, 3. "The Liquefaction of Gases," by Prof. Dewar, F.R.S.
— Institute of Electrical Engineers, 8.
— Chemical, 8. "The Action of Nitrosyl Chlorides on Amides," by Prof. Tilden, F.R.S., and Dr. M. O. Forster. "The Action of Nitrosyl Chloride on Asparagine and Aspartic Acid; Lævo-rotatory Chlorosuccinic Acid," by Prof. Tilden, F.R.S., and H. J. Marshall. "On a Property of the Non-luminous Atmospheric Coal-Gas Flame," by L. T. Wright. "A Constituent of Persian Berries," by A. G. Perkin and J. Geldard. "Potassium Nitrosulphate," by E. Divers, F.R.S., and T. Haga. "Di-ortho-Substituted Benzoic Acids," "Hydrolysis of Aromatic Nitriles and Acid Amides," and "Action of Sodium Ethylate on Deoxybenzoin," by J. J. Sudborough, Ph.D.
Friday, 26th.—Royal Institution, 9. "The Effects of Electric Currents in Iron on its Magnetisation," by John Hopkinson, F.R.S.
— Physical, 5. "A Theory of the Synchronous Motor," by W. G. Rhodwell. "Note on a Simple Graphic Interpretation of the Determinantal Relation of Dynamics," by G. H. Bryan.
Saturday, 27th.—Royal Institution, 3. "English Music and Musical Instruments of the 16th, 17th, and 18th Centuries," by Arnold Dolmetsch.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1848.

SCIENTIFIC USES OF LIQUID AIR.*

By Professor DEWAR, M.A., LL.D., F.R.S.

(Concluded from p. 194).

Seeing that the most powerful chemical affinities are in abeyance at very low temperatures, it is a matter of great interest to ascertain what change comes over the physical force we name cohesion. Here we are dealing with the molecular forces which are effective in uniting together the particles of solid bodies, in contrast to the force we name chemical attraction, which exists most characteristically between dissimilar molecules. Both are alike in this respect, that they are insensible at sensible distances. If we accept the theory of matter which regards finite heterogeneousness of the most homogeneous bodies as proved, then Lord Kelvin has shown that gravitation alone would account for the so-called cohesive forces. Thus, he says ("Popular Lectures," vol. i., p. 60):—"But if we take into account the heterogeneous distribution of density essential to any molecular theory of matter, we readily see that it alone is sufficient to intensify the force of gravitation between two bodies placed extremely close to one another, or between two parts of one body, and therefore that cohesion may be accounted for, without assuming any other force than that of gravitation, or any other law than the Newtonian." Another view of the cohesive forces is taken by Mr. S. Tolver Preston, in his work entitled "Physics of the Ether," p. 64. He says, "The phenomena of 'cohesion,' 'chemical union,' &c., or the general phenomena of the aggregation of molecules, being dependent on the molecular vibrations as a physical cause, it would therefore be reasonable to conclude that variation of vibrating energy (variation of 'temperature') would have a most marked influence on these phenomena, as is found to be the fact. Further, since when a physical cause ceases to exist the effect also ceases, it follows that at the absolute zero of temperature (absence of vibrating energy) the general phenomena of 'cohesion,' including the aggregation of molecules in chemical union, would cease to exist." If this theory is pressed so as to include the gaseous state, then at the temperature of −274° C. we may imagine the particles reduced to an incoherent layer of dust or powder. The experimental facts do not, however, warrant this conclusion, seeing that at the lowest temperature reached, which is about −210° C., air remains a transparent jelly. That a low temperature causes profound changes in the elastic constants of a metallic body is most easily shown by placing a rod of fusible metal in liquid air, and comparing the deflection produced by a weight when the rod is supported at one or both ends before and after cooling.

The Young modulus is increased to between four and five times its amount at ordinary temperatures. In the same way, the rigidity modulus can be shown to be greatly changed by cooling a spiral spring made of fusible metal wire. Such a spring at the ordinary temperature is quickly drawn out into a straight wire, by attempting to make it support an ounce weight. The same spiral, cooled to −182° C., will support a couple of pounds, and will vibrate like a steel spring so long as it is cool. In the same way, a bell or tuning-fork of fusible metal gives a distinct metallic ring at −180°. If two tuning-forks are taken of identical pitch, and one cooled to −182°, then on simultaneously striking them beats are very distinctly heard. The simplest plan of getting some idea of the change in the cohesive force at low temperature, is to ascertain the tenacity or breaking stress of the metals and alloys under such conditions, and to compare such results with similar experiments made at the ordinary temperature with the same metallic samples, using the same apparatus. In this way the comparative values are reliable. The only difficulty is the large quantity of liquid air or oxygen required to cool the steel supports of the wires, which have to be broken. Seeing that wires less than 1-10th inch in diameter are unreliable, good strong rigid steel supports are needed, and, as these have to be cooled each time a wire is broken, the experiments involve large quantities (gallons) of liquid air and oxygen. Further, as not less than three, and in many cases six experiments must be made with each sample of wire, and the stress in each case can only be applied slowly, work of this kind extends over long periods of time, and this means increased waste of liquid gases. Fig. 6 shows the general plan of the part of the testing-machine which supports the wires

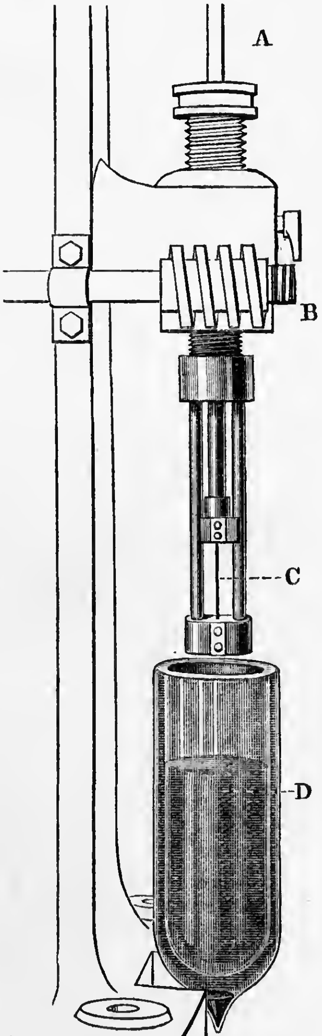

Fig. 6.

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* A Lecture delivered at the Royal Institution, Jan. 19th, 1894. (By an error this date was given in our last number as 1895, instead of 1894).

which have to be broken. In the figure, A is the steel rod which is connected to the multiplying levers, the stress being gradually increased as usual by running in water into a vessel hung from the long end of the lever; C is the wire to be tested, B is an arrangement which measures roughly the extension of the wire, and D is a large silvered vacuum vessel holding the liquid oxygen. This latter vessel must be large, in order to avoid any part of the supports of the wire coming into contact with the sides, otherwise the shock of the wire on breaking shatters the vacuum bulb. The rupture must be made while the wire is immersed in the liquid oxygen, and the whole of the supports thoroughly cooled down. The wires must be caught in long V-shaped grooves made in the steel supports in order to avoid slipping, and change in the cross section of the wire. As a rule, the wires used were $\frac{1}{10}$ inch in diameter and 2 inches long. The following table gives the mean results of a large number of experiments:—

Table I.—*Breaking Stress in Pounds of Metallic Wires* 0·098 *Inch Diameter.*

	15° C.	−182° C.
Steel (soft)	420	700
Iron..	320	670
Copper	200	300
Brass	310	440
German silver	470	600
Gold	255	340
Silver	330	420

An inspection of this table proves that all the common metals and alloys increase in tenacity at low temperatures: thus iron has doubled its breaking stress, and the other metals and alloys are all increased from a third to a half the normal amount. This increase of strength is solely due to the low temperature, and persists only during its continuance. Wires that have been cooled to the temperature of −182° C., and allowed to regain the ordinary temperature, are in no way changed as regards their breaking stress.

A second series of experiments were made with a set of cast test-pieces of metals and alloys. The test-pieces, all cast in the same mould, were 2 inches long with ½-inch spherical ends, the cylindrical portion being $\frac{2}{10}$ inch diameter. The spherical ends of the test-pieces rested in similar cavities made in a special set of steel supports that fitted on to the testing-machine. Crystalline metals give castings that are far from uniform one with another, and it is very difficult to get even comparable results with metals like zinc, bismuth, and antimony. The following table gives the experimental results:—

Table II.—*Breaking Stress in Pounds of Cast Metallic Test-Pieces. Diameter of Rod* 0·2 *Inch.*

	15° C.	−182° C.
Tin	200	390
Lead	77	170
Zinc	35	26
Mercury..	0	31
Bismuth..	60	30
Antimony	61	30
Solder	300	645
Fusible metal (Woods)	140	450

It will be noted that in this list the breaking stress, by cooling to −182° C., has been increased to three times its usual value in the case of fusible metal, and to twice its usual value in the case of tin, lead, and solder. The results with zinc, bismuth, and antimony are exceptional, seeing they appear to be diminished in tenacity. This, however, may be only apparent, because the stresses set up in cooling such highly crystalline bodies probably weaken some set of cleavage planes so that rupture is then comparatively easy. In any case it must be admitted that no reliance can be placed on the tenacity of highly crystalline metals. The breaking stress of mercury is interesting, and turns out to be at −182° C. nearly half that of lead at the ordinary temperatures. The percentage elongation is not given in the foregoing tables, simply because the value of such measurements is of little importance when such short pieces of the metals are under observation. The general results of such observations are, however, interesting: thus lead and tin at ordinary temperatures elongate before breaking about the same amount, whereas if tin is cooled to −182° C. it hardly shows any extension, and lead under such conditions shows no change, stretching as much at −182° as at 15° C. Solder and fusible metal stretch less, and the cross section of the break is much less at −182° than at 15° C. The above experiments can only be considered as preliminary to a more elaborate investigation of the actual variation of the elastic constants at low temperatures. It will require complex experimental arrangements to get reliable measurements of the Young modulus and the rigidity modulus at the temperature of boiling liquid air. In the case of fusible metal, a first attempt to compare the ratio of the Young modulus at 15° and −182° with the ratio of the rigidity modulus between the same limits of temperature, has resulted in finding that both constants are increased in the same proportion. From this it would follow that the resistance to compression of the substance at −182° C. must be increased in a similar ratio. The comparative behaviour of strong steel spirals at 15° C. and −182° as to their elongation on the repeated addition of the same load was a subject examined on several occasions. The most careful comparison of such spirals, however, revealed no measurable differences in their elongation between the ordinary temperature and that of boiling oxygen. This may be due to the want of sufficient sensibility in the testing-machine when applied to such delicate experiments. In the meantime it is reasonable to conclude that the rigidity modulus of very hard steel is not much changed by cooling it to −182° C. If balls of iron, tin, lead, or ivory are cooled to −182° C., and dropped from a fixed height on a massive iron anvil, the elastic rebound is markedly increased in all cases. The flat distortion surface produced on the lead sphere after impact is only one-third the diameter of the circular surface produced at the ordinary temperature when the lead ball falls from the same height.

The examination of the magnetic condition of matter at low temperatures is a subject of great interest and offers a wide field for investigation. In a former lecture the magnetic properties of liquid oxygen and air were discussed. Owing to the experimental difficulties, accurate quantitative measurements of the permeability have not yet been successful. Faraday was the first experimenter who examined the magnetic condition of matter at the lowest temperature that could be commanded in his time, viz., about −110° C. He did not succeed in making any substance which was non-magnetic at ordinary temperatures assume the magnetic state at the lowest temperature of the solid carbonic acid ether bath *in vacuo*. Later experimenters have directed their attention more especially to the action of high temperatures on magnetism, and the work of Professors Hopkinson and Ewing in this field of research is well known. Professor Trowbridge examined the effect of a temperature of −80° C. on a permanent magnet, and came to the conclusion that the magnetic moment was diminished by about 50 per cent. Professor Ewing found that an increase of temperature of 150° C. above 10°, caused a reduction of the magnetic moment of a bar magnet by about 40 per cent, and that the magnet on cooling recovered its original state. This result would lead us to expect that if the same law is followed below the melting-point of ice as Ewing found above it, then a bar magnet cooled to −182° C. ought to gain in magnetic moment something like 30 to 50 per cent. The experiment of Professor Trowbridge is, however, apparently opposed to such an inference. It appears, however, that Professor Trowbridge cooled a magnet that had not reached a constant state (that is to say, one that on heating would not have completely recovered its magnetisation on cooling), because after the magnet had been cooled to −80° on regaining the ordinary temperature, it had lost 50 per cent of its original magnetic moment. Such a magnet would apparently diminish in magnetic moment on cooling and heating the first time the action was examined, but a repetition of the process when the action of magnetisation and temperature were strictly reversible might lead to an opposite conclusion. To settle this question a series of experiments on the magnetic moment of small magnets cooled to −182° were carried out. Small magnets from half an inch to an inch in length were made of watch-spring or steel wire and were either used separately or in bundles; they were fixed rigidly in a block of wood by means of copper staples, and in this condition were easily clamped firmly in the field of a magnetometer. The cooling was effected by applying a cotton-wool sponge of liquid air. The relative deviations of the magnetometer are proportional to the magnetic moment of the magnet under the respective conditions of +15° and −182° C. After the first cooling the magnet is allowed to regain the ordinary temperature, and the operation of cooling and heating is repeated three or four times. The following table gives some of the results, and these may be taken as typical of a large additional number unrecorded.

If the experiment marked (1) is examined we find cooling to −182° in the first cycle produced no change of magnetic moment, but that on heating to +15° C. the magnet had lost 30 per cent of the original strength. In the second cycle cooling increased the magnetic strength of the magnet, in the condition in which it is left after the first cooling by 33 per cent, and heating diminished it by 5 per cent; whereas in the third cycle cooling showed 36 per cent increase and no loss in heating. It was only after three alterations of temperatures from +15° to −182° C. that the magnet reached a steady condition. In experiment (3) the first cooling shows a loss of 24 per cent, while in experiment (4) the first cooling shows a gain of 12½ per cent.

Change of the Magnetic Moments of Permanent Magnets at +15° and −182° C. per cent of the Value at the beginning of each Cycle, which is always 15°.

	−182° C.	+15° C.
(1) Hard steel, 0·5 inch long and 0·4 inch diameter—		
First cycle	+0	−30
Second „	+33	−5
Third „	+36	0
(2) Soft steel—		
First cycle	+12	−28
Second „	+51	0
Third „	+51	0
(3) Hard steel, 1·03 inch long, 0·4 diameter—		
First cycle	−24	−43·4
Second „	+23	0
Third „	+23	0
(4) Nine steel wires in bundle—		
First cycle	+12·5	+3
Second „	+38	−2
Third „	+33	0
Tested four days after—		
First cycle	+50	0

It is clear, therefore, that according to these experiments, every magnet has individual characteristics that may either result in no change on cooling or the addition or subtraction of from 12 to 24 per cent in the magnetic strength. All the experiments, however, show that a repetition of the cycle of heating and cooling brings the magnet to a steady state, in which cooling always causes increase in the magnetic strength of from 30 to 50 per cent, and the re-heating brings about no loss in the original magnetic moment. Such a marked alteration of magnetic strength might be used as a thermometer in low temperature research, and it is my intention to extend the enquiry to the lowest temperature that can be reached by the evaporation of nitrogen in vacua. A simple mode of showing the sudden alteration of magnetic strength on cooling is to surround a permanent magnet made up of a bundle of steel wires with a coil of copper wire, leaving the ends of the magnet to project so that they can be dipped in liquid air. When the copper wires are attached to a galvanometer, and one of the ends of the magnet cooled, an induced electrical current occurs, due to the sudden magnetic change. Accurate observations must be made on the permeability and susceptibility of the magnetic metals at the temperature of boiling liquid air, and the above results are an indirect guarantee that this field of investigation will be fruitful in new scientific facts.

This lecture has already covered a very wide field. It is easy to put into a Friday evening discourse the work of a year. Members and friends have chiefly contributed to the Research Fund, which has enabled the Institution to extend the experimental plant needed for the prosecution of research in this field of enquiry, and they have strong claims to learn, in the first instance, the results of the general laboratory work. My object has been to illustrate the scientific uses of liquid air. To do this with any satisfaction requires what may be called a good deal of scientific prospecting. It is one thing to discover where the ore lies, it is another thing to produce the refined metal. Investigations on the properties of matter at the temperature of boiling liquid air, must be in the first instance rather qualitative than rigidly quantitative. In my opinion scientific progress is best served by conducting the enquiry on these lines. It will be easy to refine later on.

I have to acknowledge the great assistance I have received in the conduct of these experiments from my excellent chief assistant, Mr. Robert Lennox, and I must also express commendation of the way Mr. Heath has helped in the work.

TERRESTRIAL HELIUM ?

Professor J. Norman Lockyer, F.R.S., writes in the current number of *Nature* as follows:—

"I have received the following letter and enclosure from Prof. Thorpe:—

"'University of Glasgow, April 16.

"'My dear Lockyer,—The enclosed extract from a letter just received from Clève of Upsala may be of interest to you.

"'Ever yours,
"'T. E. Thorpe.'"

"'I have got from Mr. Crookes a letter in which he informs me that the gas in Clèveite contains the long-searched for helium.

"This letter arrived exactly the very day one of my pupils, Mr. Langlett, tried to get the gas of Clèveite in my laboratory. The gas given off from my mineral did not contain a trace of argon. The spectrum has been examined by Thalén, who found an exact coincidence of the line of the gas with the helium line and besides some others:—

Wave-length.		Intensity.
6677	.. .. ..	Half-strong
5875·9	.. .. ..	Strong: helium
5048	.. .. ..	Half-strong
5016	.. .. ..	Strong
4922	.. .. ..	Half-strong
4713·5	.. .. ..	Weaker.

"'I have sent a letter about it to Berthelot. If you like, you may communicate the result to the Chemical Society, Mr. Ramsay, Crookes, and other friends. . . . An experiment to determine the specific gravity did not give satisfactory results, but seems to indicate that it is a very light gas, still more heavy than hydrogen. Will this gas fill the gap between hydrogen and lithium? It will become very interesting to see. What makes me much curious is, that our helium gas was free from argon, and that Mr. Ramsay's (according to *Comptes Rendus*) did contain that curious stuff. Is there any relation between argon and helium, and are we facing a new epoch in chemistry?'

"Although my results are not yet complete for publication, the foregoing communication makes it desirable that I should state at once that immediately on the publication of Prof. Ramsay's statement, by the kindness of Mr. L. Fletcher I was enabled to study the gases given off by Clèveite by heating *in vacuo*, a method I have used for metals and meteorites.

"A very small quantity of Clèveite is all that is necessary to obtain a considerable volume of the new gas, which comes off associated with hydrogen.

"I have now examined several tubes. I have found no argon lines; I have not found the lines, other than the yellow one, given by Crookes; but lines have been recorded near some of the wave-lengths given by Thalén, especially the one at 6677, near a line I discovered in the chromosphere in 1868. So far the sky has not been clear enough to enable me to determine by direct comparison with the chromospere the position of the line in the yellow with great dispersion."

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending March 31st, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, April 10th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 167 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 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 as far as possible, 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.

Of the 167 samples examined four were recorded as "clear but dull," the remainder were clear, bright, and well filtered.

With the improved meteorological conditions the London waters are approaching a state of considerable purity. In our report for the month of March last year we commented on the then excellent quality of the waters, and said that they were "rapidly approaching their high summer standard." The following comparison between the present month's supply and that of March, 1894, will show that the former high degree of analytical purity has been more than maintained.

Comparison of the Averages of the Five Thames-derived Supplies for the Months of March, 1894 *and* 1895.

	Common Salt. Per gall. Means.	Nitric Acid. Per gall. Means.	Hardness. Degrees. Means.	Oxygen. reqd. Per gall. Means.	Organic Carbon. Per gall. Means.	Colour. Br'n: Blue. Means.
Mar., 1894	2·285	1·101	15·32	0·052	0·121	21·3:20
„ 1895	2·130	0·937	15·12	0·043	0·117	18·2:20

Bacteriological examinations have been continued throughout the month, the process adopted being identical as regards culture medium, time of incubation, and temperature, with that we have all along pursued, in order that our results may be strictly comparable with each other at all times of the year. The filtered waters from the general wells at the Works had an average of 41 microbes per cubic centimetre, the unfiltered water containing 9236 per cubic centimetre.

The rainfall at Oxford during March has been very near the twenty-five years' mean, which is 1·59 inches. The actual fall was 1·46, showing a deficiency of only 0·13 inch.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

NOTE ON ANTHRACENE TESTING.

By H. BASSETT.

In the course of an experimental enquiry relating to the testing of commercial anthracene, in which I have been engaged for some months past, with the view of arriving at an improved process, some variations in the results obtained seemed to indicate the existence of an unknown cause of uncertainty in the now universally employed method, namely, Meister, Lucius, and Brüning's test of October, 1876.

In this test no reference is made to the purity of the chromic acid used.

An examination of samples of crystallised chromic acid from different sources gave percentages from 87 down to 71! and showed, moreover, the presence of sulphuric acid in quantities of from 8 to 18 per cent! The gradual draining which would occur in a large bottle containing, say, ten or twelve pounds of chromic acid would obviously increase the percentage of sulphuric acid in the lowest portion, which would be very different in quality from that first taken out for use.

Under these circumstances it appeared very surprising that anything like concordant results in testing should be possible, while experience has shown a fair agreement to be the rule; but in the course of experiment this difficulty was in great measure explained; still, however, leaving no doubt that the variations in the quality of the chromic acid have caused the occasional discrepancies which could not be accounted for.

A series of comparative tests was therefore made with different samples of anthracene, using pure chromic acid, with and without the addition of sulphuric acid, but otherwise under precisely similar conditions. The table following is an example of the results obtained.

	1. B quality.	2.	3.	4. A quality.
15 grms. chromic acid ..	32·44	34·75	39·93	51·15
10 „ „ ..	33·98	36·34	41·13	51·53
10 grms. chromic acid + 1·8 grms. sulphuric acid ..	33·26	35·05	40·36	51·06
10 grms. chromic acid + 2·8 grms. sulphuric acid ..	33·21	35·01	40·27	51·10

The points worthy of notice in the above are:—

1. That a large deficiency in the amount of chromic acid gives, as might be expected, a considerably higher percentage of anthracene.
2. That the presence of sulphuric acid appears to compensate to a great extent for the deficiency in the chromic acid, and this is doubtless the explanation of the fact before referred to as to the usually fair agreement of tests.
3. That a considerable variation in the quantity of sulphuric acid has very little influence on the results.
4. That a good A quality anthracene is only slightly affected by considerable variations in the method of testing.

This last point is confirmed by the results already obtained by my modified process, from which I anticipate good results, and which I hope to publish on the completion of experiments now in progress with a representative series of commercial samples.

36a, St. Andrew's Hill,
Queen Victoria Street, E.C.

THE CAUSE OF LUMINOSITY IN THE FLAMES OF HYDROCARBON GASES.*

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

(Concluded from p. 192).

It is perfectly possible for the temperature of a flame to be so little above the point necessary to decompose the diluted acetylene that, whilst some decomposes and renders the flame faintly luminous, the larger portion burns without decomposition. A good example of this is to be found in the combustion of alcohol, the flame of which contains as much acetylene as is to be found in a good coal-gas flame, but which is practically almost non-luminous. If alcohol in a small dish be ignited, it burns with a faintly luminous flame, and if a bell-jar is placed over it some of the products of combustion mingling with the flame still further cool it and render it non-luminous; but if now a stream of oxygen be introduced under the bell-jar, the temperature of the flame is at once increased and becomes highly luminous, whilst a cold porcelain vessel held in the flame is coated with soot.

In all the experiments in which light was developed in heated tubes by the decomposition of acetylene, the glow of the carbon was red and lurid, the light emitted being of the same character and appearance as that developed by the combustion of potassium in carbon dioxide, and entirely lacking the pure white incandescence of the acetylene flame as burnt from a flat-flame burner.

This may be due to the fact that in the open flame the temperature of the carbon particles is presumably due to three sources of heat:—

A. Heat derived from the decomposition of the acetylene molecule.
B. Heat derived from the combustion of hydrogen, carbon monoxide, and some hydrocarbons in the flame.
C. Heat derived from the combustion of the carbon particles themselves.

Whilst in the tube experiments the heat of the walls of the tube and the heat of decomposition alone are acting, and it is evident that the intensity of the heat finding its way through the walls of the tube will be very different to that exercised by the walls of burning gas which enclose the luminous portion of the flame, and there can be but little doubt that the temperature of the carbon particles will vary enormously with the rate at which the acetylene decomposes, as the more quickly the action takes place the greater will be the localising action upon the heat evolved, and the higher the incandescence of the carbon particles.

That this is so seems certain from the whiteness of the flash of light emitted when the acetylene is detonated; and experiments were made in order to, if possible, gain an idea as to how much of the incandescence of the carbon particles was due to the endothermicity of the decomposing acetylene, and how much to the action of heat and combustion on the carbon particles after formation.

In order to do this a non-luminous flat flame of large size was desired, and was obtained by using coal-gas de-illuminated by slowly passing it through bromine, well washing with sodic hydrate solution and water, and then passing it through strong sulphuric acid, the gas so treated having an illuminating value of 1·2 candles for 5 cubic ft. when burnt in the London argand at such a rate as to give a 3-inch flame, whilst in a fish-tail burner it gave a non-luminous flame. This gas gave on analysis the following percentage composition:—

Carbon dioxide	0·00
Unsaturated hydrocarbons..	0·00
Carbon monoxide	5·50
Saturated hydrocarbons ..	33·28
Hydrogen	55·25
Nitrogen	5·49
Oxygen	0·48
	100·00

So that its combustion would give practically the same temperature and flame reactions as those in an ordinary gas-flame.

A very fine platinum tube was now obtained, closed at one end, and with five minute holes bored in a line close to the sealed end; and this having been so arranged that the holes were buried in the flame just at the top of the inner zone, acetylene was then gently allowed to flow through them into the flame.

At the points where the acetylene issued into the flame, small areas of intense luminosity were produced, whilst the liberated carbon streaming up between the flame walls of the upper zone produced dull red bands of very low luminosity. It may be suggested that the carbon particles supplied in this way to the flame may have agglomerated and formed masses larger than those produced in the ordinary way; but I do not think this, as they were completely consumed, and no smoke escaped from the crown of the flame, whereas if a flat flame is interfered with in such a way as to cause the carbon particles to roll themselves together, smoking of the flame is produced.

I think the inference to be drawn from this experiment undoubtedly is that it is the heat of decomposition which gives the high incandescence and light emitting value to the carbon particles, and that the temperature of the combustion of the other flame-gases, and finally of the carbon itself, plays but a secondary part.

In considering these results, it seems remarkable that if acetylene owes its power of rendering hydrocarbon flames luminous to its high endothermic properties, that cyanogen, which is still more endothermic, should burn under all conditions that have at present been tried with a non-luminous flame.

		Heat of Formation.
Acetylene	C_2H_2	−47,770
Cyanogen	C_2N_2	−65,700

It is clear that if the rapidity of decomposition localises the heat evolved to the products of decomposition, and that this renders the liberated carbon particles incandescent, whilst the hydrogen plays at best a very subsidiary part, it ought not to matter whether it be hydrogen or nitrogen which is combined with the carbon.

Berthelot showed that cyanogen, like acetylene, could be detonated by a small charge of mercuric fulminate; but he notes that the test is not always successful, which points to the decomposition of this body requiring a

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* A Paper read before the Royal Society.

greater expenditure of energy to break up the molecule than is the case with acetylene, and known facts would lead us to expect that this would be the case, as although exothermic compounds become less and less stable with rise of temperature, endothermic bodies, on the other hand, become more stable, and the endothermicity of cyanogen being greater than that of acetylene, would lead one to expect that temperatures which would decompose acetylene would have no effect on cyanogen, and that, as during the combustion of cyanogen, the liberation of nitrogen would probably have a diluting and cooling action, the cyanogen would burn directly without liberating any carbon which could emit light.

In order to see if the temperature of the cyanogen flame, when burnt from an ordinary flat-flame burner, differed much from that of hydrocarbons when consumed in a flame of the same size and kind, the temperatures were experimentally determined by the same method employed, and in the same parts of the flame, as had before been done with acetylene, ethylene, and coal-gas.

Portion of the Flame.	Temperature.
Centre of inner zone ..	1377° C.
Top of inner zone.. ..	2085
Near top of outer zone..	1645

Showing that the cyanogen flame was actually hotter than the acetylene and ethylene flames, and about the same as the coal-gas flame, but that the heat was differently distributed, the inner zone being far hotter than in the other gases, whilst the maximum temperature of the flame was at the apex of the inner zone, instead of being nearer the top of the flame.

An experiment was now made to ascertain if it were possible to decompose cyanogen with luminous deposition of carbon, by passing it through a hard glass tube heated by means of the blowpipe; but at the highest temperature attainable no trace of any deposition of carbon took place, showing how far more stable cyanogen is under the influence of high temperatures than acetylene.

The structure and characteristic appearance of the cyanogen flame have been explained by Smithells (*Chem. Soc. Journ.*, 1894, p. 603) and Dent, who conclude that the inner zone of peach blossom tint is caused by the combustion of the cyanogen to carbon monoxide and nitrogen, whilst the outer blue cone is formed by the oxidation of the monoxide to dioxide, the green fringe to the outer cone being attributed to the presence of small quantities of oxides of nitrogen; and if this explanation be accepted, it is clear that we could not obtain luminosity in the portion of the flame immediately above the inner zone, as all cyanogen has been destroyed without decomposition before that point is reached. It is conceivable, however, that although no luminosity can be detected in a cyanogen flame, and although the temperature which can be obtained in a glass tube is insufficient to break up the compound with luminous separation of carbon, yet if cyanogen could be heated to a considerably higher temperature, it might be possible to decompose it in such a way as to develope luminosity.

In order to try this point a hydrogen flame was burnt from the end of an open platinum tube 9 m.m. in diameter, and a thin platinum tube 2·5 m.m. in diameter was passed up through the broad tube to the apex of the inner zone, and a slow stream of cyanogen was admitted, with the result that the flame at once became luminous, and on surrounding the hydrogen flame with an atmosphere of oxygen to increase the temperature, the luminosity was considerably increased.

This experiment at once explains the cause of the non-luminosity of the cyanogen flame, and shows that it is purely a question of temperature, and the probabilities are that, burnt in a flame which gave sufficient heat to rapidly decompose it, nearly as high an illuminating value as that of acetylene would be obtained.

I think the explanation of the apparent anomaly of the cyanogen flame having a higher temperature than the acetylene and ethylene flames, is to be found in the fact that the molecules of cyanogen are consumed without previous decomposition, so that the heat absorbed during the formation of the cyanogen is added to the heat of combustion, and raises the average temperature of the flame, whereas with acetylene the instantaneous decomposition of the molecule before combustion confines the heat evolved to the liberated products, and the average temperature of the flame is but little more than the heat of combustion.

If the luminosity of a hydrocarbon flame is principally due to the localisation, during intensely rapid decomposition, of the heat of formation in the products, the illuminating values of such hydrocarbon gases as contain two atoms of carbon in the molecule should bear a simple ratio to their heat of formation. The gaseous hydrocarbons are—

Hydrocarbon.	Composition.	Heat Formation at Constant Pressure.
Ethane	C_2H_6	+25670
Ethylene	C_2H_4	− 8000
Acetylene	C_2H_2	−47770

And although they may undergo many changes in the flame, they will all ultimately be reduced to carbon and hydrogen again before the full luminosity of the flame is developed.

When the acetylene into which these hydrocarbons is converted by heat is decomposed, the action takes place with such enormous rapidity that one would expect the heat evolved to simply divide itself amongst the liberated atoms, so that the question of specific heat at high temperatures may be omitted.

With exothermic compounds like ethane considerable heat will have to be developed by its own combustion before it is converted into the acetylene, which, by its decomposition, endows the flame with luminosity; and if we take the ethane and call its light producing energy 1, we can then obtain a ratio of such energy for the other hydrocarbons available for distribution amongst the products of decomposition:—

$$\text{Ethane} \quad .. \quad .. \quad \frac{25670}{25670} = 1$$

$$\text{Ethylene..} \quad .. \quad \frac{25670 + 8000}{25670} = 1{\cdot}31$$

$$\text{Acetylene} \quad .. \quad \frac{25670 + 47770}{25670} = 2{\cdot}86$$

These ratios must now be divided amongst the atoms liberated at the moment of decomposition from the molecule, and we thus obtain the ratio:—

$$\begin{array}{ccccc} C_2H_6. & & C_2H_4. & & C_2H_2. \\ \frac{1}{8} & : & \frac{1{\cdot}31}{6} & : & \frac{2{\cdot}86}{4} \end{array}$$

or—

$$1 : 1{\cdot}74 : 5{\cdot}72$$

The determination of the illuminating value of a gas becomes more and more difficult the higher its illuminating value, owing to the cooling effect of the small burners that must of necessity be used in order to ensure complete combustion. Dr. Percy Frankland (*Chem. Soc. Journ.*, xlvii., p. 237) assigned the illuminating value of thirty-five candles to ethane as the mean of four tests, which varied considerably amongst themselves, and, adopting his figure, the calculated illuminating values for the ethane, ethylene, and acetylene would be—

	Illuminating Value.	
	Calculated.	Found.
Ethane	1 × 35 = 35	35
Ethylene	1·79 × 35 = 60·9	68·5
Acetylene.. ..	5·72 × 35 = 200·2	240

figures which are far nearer the experimental ones than could have been expected, considering the crude character of the calculation and insufficient data, which leads to omitting altogether such important factors as the amount of gas consumed to bring about the requisite temperature of decomposition, the specific heat of the products, and the thermal value of the change from gaseous to solid carbon, and are of no value except as showing that a ratio does exist between heat of formation and illuminating value.

Methane is the only other gaseous hydrocarbon of which the heat of formation is known, it being +21750, and as the molecule contains only one atom of carbon, two mols. have to be taken, and on calculating the probable illuminating value by the same method as was applied to the other hydrocarbons, we should have—

$$\frac{\dfrac{25670+\left\{25670-(21750\times 2)\right\}}{25670}\times 35}{10\times\frac{1}{8}}=8\cdot 4,$$

and the illuminating value, as determined by Mr. Lewis T. Wright, is 5·2; but here, again, we know by experiment that methane requires a very high temperature to bring about its conversion into acetylene and decomposition into carbon and hydrogen, and that a large portion of the gas must be burnt without decomposition to do this.

The facts which I have sought to establish in this paper are:—

1. That the luminosity of hydrocarbon flames is principally due to the localisation of the heat of formation of acetylene in the carbon and hydrogen produced by its decomposition.

2. That such localisation is produced by the rapidity of its decomposition, which varies with the temperature of the flame and the degree of dilution of the acetylene.

3. That the average temperature of the flame due to combustion would not be sufficient to produce the incandescence of the carbon particles within the flame.

In my paper on the action of heat upon ethylene, brought before the Royal Society this spring, I showed that the decomposition of ethylene into acetylene and simpler hydrocarbons was mainly due to the action of radiant heat, and was but little retarded by dilution, whilst I have shown in this paper that the acetylene so produced requires a considerable increase in temperature to bring about its decomposition when diluted, and it is possible with these data to give a fairly complete description of the actions which endow hydrocarbon flames with the power of emitting light.

When the hydrocarbon gas leaves the jet at which it is being burnt, those portions which come in contact with the air are consumed and form a wall of flame which surrounds the issuing gas. The unburnt gas in its passage through the lower heated area of the flame undergoes a number of chemical changes, brought about by the action of radiant heat emitted by the flame walls, the principal of which is the conversion of the hydrocarbons into acetylene, methane, and hydrogen. The temperature of the flame quickly rises as the distance from the jet increases, and a portion of the flame is soon reached at which the heat is sufficiently intense to decompose the acetylene with a rapidity almost akin to detonation, and the heat of its formation, localised by the rapidity of its decomposition, raises the liberated carbon particles to incandescence, this giving the principal part of the luminosity to the flame; whilst these particles, heated by the combustion of the flame gases, still continue to glow, until finally themselves consumed, this external heating and final combustion adding slightly to the light emitted.

Any unsaturated hydrocarbons which have escaped conversion into acetylene before luminosity commences, and also any methane which may be present on passing into the higher temperatures of the luminous zone, become converted there into acetylene, and at once being decomposed to carbon and hydrogen, increase the area of the light-giving portion of the flame.

My thanks are due to Mr. F. B. Grundy for the help he has given me in the work entailed by this paper.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1895.

Dr. Armstrong, President, in the Chair.

(Concluded from p. 197).

*38. "*β-Ethoxynaphthalenesulphonic Acids. The Arrest of Isomeric Change at an Intermediate Stage.*" By Arthur Lapworth,

Armstrong and Amphlett have shown (*Proc. Chem. Soc.*, 1887, 147) that when a solution of β-ethoxynaphthalene in carbon bisulphide is sulphonated by means of chlorosulphonic acid, at the ordinary temperature, two sulphonic acids are formed, one of which—the minor product—was proved to be 2 : 3′-ethoxynaphthalenesulphonic acid; they expressed the opinion that the major product was probably the 2 : 1′-acid, and showed that when the original product of sulphonation was heated merely on the water-bath this acid, with the greatest ease, underwent conversion into the isomeric 2 : 3′-acid.

Subsequently Percival, in like manner (*Ibid.*, 1889, 73), obtained two corresponding acids from β-methoxynaphthalene, and showed that in this case also the one was convertible into the other by mere heating on the water-bath. He, however, made the remarkable observation that one of the products (it was presumed that there were but two) was hydrolysed with extreme facility, a behaviour not noticed in the case of the ethoxy compounds.

These observations have served to suggest experiments, which the author has undertaken, at Professor Armstrong's request, with the object of extending the knowledge of such derivatives, and also of obtaining additional information as to the course of change on continued sulphonation. It was to be supposed that this would be more readily gained than in the case of β-naphthol itself, as it is possible to prepare crystalline sulphochlorides, &c., from ethoxy- and methoxy-acids, whilst the naphtholsulphonic acids can only be characterised by means of their salts. This anticipation has been fully confirmed. In the first place, Armstrong and Amphlett's inference that the chief product from β-ethoxynaphthalene is probably the 2 : 1′-acid was confirmed by ethylating 2 : 1′-β-naphtholsulphonic acid; an ethoxy-acid was thus obtained, yielding a sulphochloride, amide, and anilide identical with those derived from the unstable acid produced on sulphonating β ethoxynaphthalene at the ordinary atmospheric temperature.

2 : 1′-β-Ethoxynaphthalenesulphonic chloride,—

$$C_{10}H_7(OEt)SO_2Cl,$$

crystallises in large, shortened, monosymmetric prisms melting at 93°; the corresponding amide crystallises in needles melting at 165°; and the anilide forms magnificent orthorhombic prisms melting at 158°.

On nitrating potassium 2 : 1′-β ethoxysulphonate, it is converted into a mononitro-sulphonic *acid*, which crystallises from nitric acid in shining needles. The sulphochloride of this nitro-acid, which may also be prepared directly from the 2 : 1′-ethoxysulphochloride, melts at 155°; the amide at 173·4°.

2 : 3′-Ethoxynaphthalenesulphochloride crystallises in remarkably well-developed needles or tables belonging to the anorthic system, melting at 107·5°; the amide forms needles melting at 183°; the anilide small prisms melting at 152—153°.

1 : 2-Bromo-β-ethoxynaphthalene, which crystallises in small plates melting at 66°, yields practically nothing but 1-bromo-2 : 3'-sulphonic acid on sulphonation by means of chlorosulphonic acid. The same acid is obtained on brominating the 2 : 3'-ethoxysulphonic acid. The potassium salt of the acid is sparingly soluble in water, and is isomorphous with the corresponding β-naphthol and β-methoxy salts. The bromosulphochloride crystallises in tables melting at 131—132°; the amide in small pyramidal crystals melting at 191°.

Potassium 2 : 3'-β-ethoxynaphthalenesulphonate is converted into a sparingly soluble mononitro-*salt* on nitration. The corresponding chloride crystallises in anorthic plates melting at 146°; the amide is especially characteristic, crystallising in beautiful glistening prisms or needles melting at 218°.

2 : 2'-Ethoxynaphthalenesulphonic acid, prepared by ethylating the acid first described by Weinberg, yields a sulphochloride crystallising in plates which are either rhombic or monoclinic; it melts at 103°. The amide crystallises in needles melting at 172°. The anilide, which is the most characteristic compound, forms monoclinic pyramids of large size, melting at 153°.

On studying the products from β-methoxynaphthalene, it was found that the acid which undergoes hydrolysis so readily is not the 2 : 1'-acid, which, when separated, proved to be stable in solution; it followed, therefore, that three acids were formed, not two, as had been previously supposed, and it was probable that one of these was the 2 : 1-acid, as the corresponding naphthol acid is known to undergo hydrolysis very readily. Subsequent observations have justified this conclusion.

The chloride from the 2 : 3'-methoxy acid forms prisms which melt at 93°; an amide, crystallising in needles, which melt at 199°; and an anilide, crystallising in silky needles, melting at 79—80°.

The sulphochloride of the 2 : 1'-methoxy acid, like the corresponding ethoxy-compound, crystallises in large monoclinic prisms, or plates, melting at 137°; the amide crystallising in needles which melt at 153°, and the anilide crystallising in anorthic tables melting at 196°.

When the chlorides of these acids are heated or distilled, either alone or with phosphorus pentachloride, they do not yield the corresponding chloro-derivatives of naphthol, but either suffer complete decomposition or undergo chlorination.

On disulphonating ethoxynaphthalene at the atmospheric temperature, a very mixed product was obtained, from which it was found possible to isolate the disulphonic acids only after the expenditure of much time and labour. A surprising amount of 2·3'-salt accompanied the 2·1'-sulpho salt.

Only one disulphonic acid is formed in any appreciable quantity; this gives salts which, on the whole, are badly characterised, but yields a chloride of a well-defined character. This crystallises from benzene in large transparent monoclinic crystals which contain 1½ mol. of benzene of crystallisation, and melt when heated quickly at 51°. The chloride itself forms ill-defined plates melting at 10° C.; the amide crystallises in needles melting at 253—254°, the anilide anorthic plates melting at 127°.

In order to determine the nature of this disulphonic acid, solutions of the 2·1' and 2·3'-sulphonic chloride in warm chloroform were separately sulphonated with SO_3HCl, a novel method which has been found to afford most satisfactory results; on adding water to the products the sulphonated sulphochlorides at once dissolve, hydrolysis occurring immediately.

The 2·1'-sulphochloride yields an acid which was found to be identical with that produced on ethylating 2 : 1' : 3'-β-naphtholdisulphonic acid. Both products gave a sulphochloride crystallising in monoclinic prisms melting at 158° and the same amide and anilide.

The disulphonic acid from the 2·3'-disulphochloride on the other hand was found to be identical with the acid formed directly from ethoxynaphthalene, and as it was different from the 2 : 1' : 3'-disulphochloride the conclusion was arrived at that the constitution was EtO:S:S = 2 : 1 : 3'. If such be the case, it follows that the first product of sulphonation of ethoxynaphthalene must be the 2-1-acid.

This result therefore led the author to sulphonate ethoxynaphthalene at as low temperature as possible by adding the chlorosulphonic acid to a solution cooled by a weak freezing mixture; the product was found to consist practically entirely of the 2 : 1-acid. On allowing the product to stand, however, merely at the ordinary temperature, during only about twelve hours, it was found that it underwent change chiefly into the isomeric 2 : 1'-acid, a small proportion of the 2 : 3'-acid being also formed. As the 2 : 1-acid is very easily hydrolysed, the separation of methoxynaphthalene observed by Percival is easily accounted for.

Judging from the manner in which the 2 : 1'-acid is thus formed, it is difficult to avoid the conclusion that its production from the 2 : 1-acid is due to direct isomeric change; and if it be supposed that the production of the 2 : 3'-acid is due to further isomeric change, this would appear to be the first case in which the arrest of isomeric change at an intermediate stage has been observed.

2 : 1-Ethoxynaphthalenesulphonic chloride crystallises in long needles melting at 115—116°, its amide forms monoclinic prisms melting at 158°, and the anilide is also monoclinic, crystallising in large pyramids melting at 187°. The sulphonic group is at once displaced by the action of either nitric acid or bromine.

2 : 3 : 3'-Ethoxynaphthalenedisulphonic acid, prepared by ethylating the corresponding naphthol acid, yields a chloride crystallising in ill-defined plates melting at 121°.

It is proposed to complete the series of ethoxysulphonic acids. The behaviour of α-ethoxynaphthalene will form the subject of a later communication.

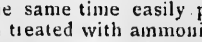
DISCUSSION.

The PRESIDENT said that it was very noteworthy that Dr. Moody had failed to corroborate the statements of all previous workers with ortho- and metaxylene, ethylbenzene, and methoxy- and ethoxybenzene, finding that none of these gave isomeric acids on sulphonation: having taken the very greatest pains to purify the materials he had used, he had not been misled by impurities. The readiness with which the ortho acids in all cases underwent change was remarkable, but most remarkable of all was the difference which he had established between methylbenzene (toluene) and ethylbenzene. The non-appearance of ortho-acid when the latter was sulphonated was probably to be accounted for by the extreme readiness with which the ortho-acid, conceivably the initial product of sulphonation, underwent "isomeric change," but whatever the explanation, the observation of so striking a difference in the behaviour of homologous methyl and ethyl derivatives was of great interest.

Mr. Lapworth's discovery that it was possible to arrest "isomeric change" at an intermediate stage was a very remarkable one; such results were of extreme importance as furnishing the materials required for the discussion of the mechanism of isomeric change.

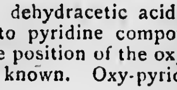
39. "*Some Oxypyridine Derivatives.*" By Miss A. P. SEDGWICK and N. COLLIE, Ph.D.

The authors have made a number of pyridine compounds from the derivatives of dehydracetic acid. The original object of the research was to produce as many oxypyridine derivatives as possible, whose constitutional formulæ would be known. Two substances, dimethyl pyrone and the lactone of triacetic acid,—



$$\begin{array}{c} CH_3{\cdot}C—O—C{\cdot}CH_3 \\ \| \qquad\quad \| \\ HC{\cdot}CO{\cdot}CH \end{array}$$

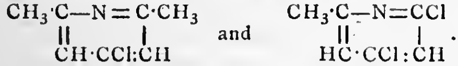
and



$$\begin{array}{c} CH_3{\cdot}C—O—CO \\ \| \qquad\quad | \\ HC{\cdot}CO{\cdot}CH_2 \end{array},$$

are not only easily prepared from dehydracetic acid, but at the same time easily pass into pyridine compounds when treated with ammonia. The position of the oxygen atoms in the pyridine ring is also known. Oxy-pyridines are substances which possess all the marked and characteristic properties of phenols and quinones, but up to the present we are only acquainted with a very few of these compounds.

The pyridine derivatives, used by the authors as a starting-point in the research, were *γ-chloro-aa'-dimethyl pyridine, and αγ-dichloro-α'-methyl pyridine,*—



$$\begin{array}{ccc} \begin{array}{l} CH_3\cdot C—N{=}C\cdot CH_3 \\ \quad\ \| \qquad\quad\ \ | \\ \quad CH\cdot CCl{:}CH \end{array} & \text{and} & \begin{array}{l} CH_3\cdot C—N{=}CCl \\ \quad\ \| \qquad\quad\ \ | \\ \quad HC\cdot CCl:CH \end{array} . \end{array}$$

By the action of dilute permanganate of potash on the first of these, two acids were obtained. The first, *γ-chloro-aa'-pyridine dicarboxylic acid*, is sparingly soluble in water, but crystallises well from acetic acid with 1 mol. of water of crystallisation; when heated it chars at about 220° without melting. A very characteristic reaction of this substance is the production of a brilliant cherry-red colouration with ferrous sulphate.

γ-Oxy-aa' pyridinedicarboxylic Acid or Chelidamic Acid.—This substance was produced from the foregoing acid by careful fusion with potash. It possessed all the properties of chelidamic acid, prepared from chelidonic acid; when it is heated to 260°, carbon dioxide is copiously evolved, *γ-oxypyridine*, m. p. 66°, being formed.

α-Methyl-γ chloro-α'-pyridinecarboxylic Acid.—This is the second acid which is produced when γ-chlorolutidine is oxidised with potassium permanganate: it is more soluble in water than the first acid. Its m. p. is 93°; it crystallises in long needles without water of crystallisation. When strongly heated it decomposes, yielding *γ-chloro-picoline*. This compound is a liquid, b. p. 162·5—163·5°. It is possibly the same as a chloropicoline noticed by Ost (*Ber.*, xvi., *Ref.*, 1374), which he obtained by reducing pentachloropicoline with tin and hydrochloric acid. When γ-chloropicoline is oxidised with permanganate of potash it is converted into *γ chloropicolinic acid*, m. p. 194—195°, and this acid when fused with potash yields *γ-oxypicolinic acid*, which melts at 263—264°. When the lactone of triacetic acid is heated with ammonia dioxypicoline is formed; the compound can be quantitatively converted into *αγ-dichloro-α'-methyl pyridine*. This chloride on oxidation with permanganate is converted into *αγ-dichloropicolinic acid*, m. p. 101—102°, which crystallises in long needles. When heated it does not yield dichloro-pyridine, but suffers complete decomposition. If it is boiled with sodium ethylate it is completely converted into *αγ-ethoxypicolinic acid*, which melts at 93—95°, and this substance yields *αγ-dioxypicolinic acid* when boiled with fuming hydriodic acid. This oxy-acid melts at 270—273°, and is isomeric, though not identical with, another dioxypicolinic acid, comenamenic acid. Several attempts were made to prepare αγ-dioxypyridine, but without success. *αγ-Diethoxypicoline* was made from dichloropicoline by boiling it with sodium ethylate. It is a sweet smelling oil, which boils between 238—240°.

40. "*On the Colouring Principle of* '*Toddalia aculeata*' *and* '*Evodia meliæfolia.*'" By A. G. Perkin and J. J. Hummel.

Toddalia aculeata is an Indian plant belonging to the Rutaceæ. Its root bark is used in Madras as a yellow dye-stuff; it also possesses valuable medicinal qualities. The authors find that the colouring matter is berberine, contrary to the statement of Flückiger and Hanbury, who were unable to detect this alkaloid.

Evodia meliæfolia, belonging to the same natural order, is a tree growing in China and Japan, whose bark is largely employed in medicine and in dyeing. The authors confirm previous statements that the bark contains berberine.

Comparative dyeing experiments on wool indicated that Evodia and Toddalia bark possess the same tinctorial power as a 3 per cent solution of berberine hydrochloride.

41. "*Some Ethereal Derivatives of Sarcolactic Acid.*" By Percy Frankland, Ph.D., B.Sc., F.R.S., and James Henderson, B.Sc.

The authors have prepared sarcolactic acid in quantity by the fermentation method previously described by Percy Frankland and MacGregor (*Trans.*, 1893, 1028). Of this sarcolactic acid they have prepared the following derivatives: methylic and ethylic sarcolactate, methylic and ethylic acetylsarcolactate, ethylic benzoylsarcolactate.

The optical and other constants determined are given in the accompanying table.

The relationship between these and the corresponding derivatives of active glyceric acid is discussed. The more important points are:—

1. The small effect on the rotation of substituting ethyl for methyl in the lactate compared with that in the glycerate.

2. The much greater increase in the rotation effected by acetylating the lactate than by diacetylating the glycerate.

3. The reversal of the sign of rotation by the introduction of the benzoyl group. This is also the effect of introducing two benzoyl groups into the glycerates.

4. The comparatively slight difference in rotation exhibited by the methylic and ethylic lactates probably points to the latter exhibiting the "maximum" in this series of ethereal salts; the maximum, as calculated from the product of asymmetry, should be exhibited by the methylic salt; in the glyceric series the calculated maximum is exhibited by the propyl, and actually by the tributyl compound. The coincidence in both cases is, therefore, probably similar.

5. The ethereal salts of glyceric acid exhibit a diminishing density in ascending the series from the methylic to butylic; the diacetylglycerates have lower densities than the corresponding glycerates, excepting in the case of the heptyl and octyl compounds, of which the diacetyl glycerates have a greater density than the corresponding glycerates, or, in other words, the density curves of the glycerates and diacetylglycerates cross at the maximum (the butyl compound). The same phenomenon is repeated in the case of the lactates; methylic acetyl-lactate has a lower density than methylic lactate; ethylic acetyl-lactate has a higher density than ethylic lactate.

6. This intersection of the density curve is also in both cases attended with a remarkable change in the optical relationship, which may be stated thus: the greater the diminution in the density effected by acetylating, the greater is the increase in the rotation produced by this constitutional change; and when the effect of acetylating is to increase the density, the increment in rotation is

Ethereal salts.	Boiling-point (uncorr.).	Relative density, 15°/15°.	Observed rotation at 15° C., α_D. (198·4 m.m. tube).	Specific rotation, $[\alpha]_D$.	Molecular rotation, $\frac{M\,[\alpha]_D}{100}$	Molecular deviation, $[\delta]_D = \frac{\alpha}{L}\sqrt[3]{\frac{M}{d}}$.	Product of asymmetry ($P \times 10^6$).
	°	°	°	°	°	°	°
Methylic sarcolactate ..	143—145	1·1017	−15·00	−6·86	−7·13	−34·4	79·16
Ethylic sarcolactate	152—154	1·0414	−17·90 (at 16·5° C.)	−8·66	−10·22	−43·7	73·84
Methylic acetylsarcolactate	170—171·5	1·0957	−94·36	−43·41	−63·38	−242·9	0
Ethylic acetylsarcolactate	179·5—180·5	1·0327	−86·62	−41·47	−66·35	−232·9	198·6
Ethylic benzoylsarcolactate	154—155·5 (15 m.m.)	1·1164 (14·9°/14·9°)	+49·2	+22·22	+49·33	+144·7	416·2

markedly less than in those cases in which the density is diminished by the process. This applies also to both glycerates and lactates.

7. The effect of benzoylating is to increase the density, whilst at the same time it enormously diminishes the rotation, as well as reversing the sign of the latter. This again holds good for both glycerates and lactates.

42. "*Electrolysis of Potassium Allo-ethylic Camphorate.*" By James Walker, D.Sc., and James Henderson, B.Sc.

The chief products obtained on electrolysing potassium allo-ethylic camphorate are the ethylic salts of an unsaturated acid, $C_9H_{14}O_2$, and of a dibasic saturated acid, $C_{18}H_{30}O_4$. These acids have been named *allo-campholytic* and *allo-camphothetic* acids respectively. The former acid gives a liquid dibromide, and can be converted into the isomeric campholactate of Fittig and Woringer. It is not identical with lauronolic acid, which also yields campholactone on similar treatment. The isolauronolic acid of Kœnigs and Hœrlin is identical with isocampholytic acid. The results obtained indicate that camphoric acid contains the group $\cdot\dot{C}H\cdot CH(COOH)\cdot\dot{C}(COOH)$.

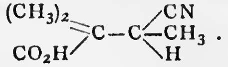
43. "*Trimethylsuccinic Acid.*" By W. A. Bone, M.Sc., Ph.D., and W. H. Perkin, jun., Ph.D., F.R.S.

For some time the authors have been working with this acid and the isomeric dimethylglutaric acids, and, although their experiments are not yet complete, the recent appearance of a paper by Auwers on the same subject (*Ber.*, xxviii., 263) renders the publication of this short notice necessary.

There has been a good deal of discussion as to whether trimethylsuccinic acid exists in one or two modifications. The authors have prepared this acid by two different methods, viz. (1) by the action of ethylic α-bromisobutyrate on the sodium derivative of ethylic α-cyanopropionate (Zelinsky, *Ber.*, xxiv., 468); (2) and by the action of ethylic α-bromisobutyrate on the sodium derivative of ethylic methylmalonate dissolved in xylene at 180° (Bischoff, *Ber.*, xxiv., 1041). The products were in each case hydrolysed, and the acid heated at 200°. The authors find that one and the same trimethylsuccinic acid is always formed, and that when pure this melts at 152°; and they are able to confirm the results recently obtained by Auwers, which differ materially from those described by Zelinsky (*Ibid.*), Bischoff (*Ibid.*), and Hell ("Inaug. Diss.," Bonn, 1893).

Trimethylsuccinic acid is characterised by yielding a very insoluble calcium salt, which affords a convenient method for separating it from the isomeric dimethylglutaric acids, which are always formed in the above interactions. When heated with acetic anhydride, trimethylsuccinic acid yields an anhydride melting at 38—39°.

During the course of their experiments, the authors have also obtained cyanotrimethylpropionic acid,—



$$(CH_3)_2(CO_2H)C-C(CN)(CH_3)H \, .$$

This acid crystallises in colourless needles, melting at 126°, and it is characterised by yielding a sparingly soluble ammonium salt, which crystallises from water in long colourless needles. Acetic anhydride converts cyanotrimethylpropionic acid into a crystalline substance melting at 65°, which is at present under investigation. On hydrolysis with concentrated hydrochloric acid, cyanotrimethylpropionic acid yields trimethylsuccinic acid, which shows that it must have the constitution represented above.

A description of the results recently obtained in the investigation of the isomeric symmetrical dimethylglutaric acid, which is not yet concluded, is reserved for a future paper.

44. "*New Isomeric Sulphonic Chlorides derived from Camphor.*" By F. Stanley Kipping, Ph.D., D.Sc., and William J. Pope.

In our first paper on the sulphonic derivatives of camphor (*Trans.*, 1893, lxiii., 548) the separation of dextrorotatory camphor sulphonic chloride and of the corresponding optically inactive compound was described, and it was mentioned that the crude oily product obtained by the interaction of sodium camphorsulphonate and phosphorus pentochloride contained other crystalline compounds of unknown composition. As it seemed possible that these by-products might prove to be interesting derivatives of camphor, their investigation has been continued; two new crystalline substances have now been isolated from the mixture.

The compounds in question are isomeric sulphonic chlorides of the composition $C_{10}H_{14}Cl\cdot SO_2Cl$, and both are optically inactive; we propose for the present to call them *chlorocamphenesulphonic chlorides*, at any rate until further study shows that they are not, as we believe them to be, camphene derivatives.

α-Chlorocamphenesulphonic chloride may be obtained in beautiful, massive, transparent crystals, but it is much more readily soluble than either of the camphorsulphonic chlorides in all ordinary solvents, and dissolves freely even in boiling light petroleum (b. p. 40—50°); it melts not quite sharply, at 83—84°, and appears to be dimorphous, as, when the liquefied substance is rapidly cooled, it solidifies to an opaque mass which does not melt until 86—87°.

α-Chlorocamphenesulphonamide, $C_{10}H_{14}Cl\cdot SO_2\cdot NH_2$, is obtained on shaking the sulphonic chloride with cold concentrated ammonia; it crystallises from dilute alcohol in transparent plates melting at 161—162°, and is only sparingly soluble in water.

α-Dichloracamphene, $C_{10}H_{14}Cl_2$, is formed in large quantities when α-chlorocamphenesulphonic chloride is heated for a short time at 160—170°; it crystallises from dilute alcohol in fern-like forms melting at 72—73°, and is readily volatile in steam.

β-Chlorocamphenesulphonic chloride appears to be present in the crude oily product in much smaller quantities than the corresponding α-compound, and, being much more readily soluble than the latter, it is isolated only with difficulty; it dissolves freely even in cold light petroleum (b. p. 30—40°) from which it crystallises in large, transparent plates which become opaque when heated gently in contact with the mother-liquor; its melting-point is 77—78°.

β-Chlorocamphenesulphonamide, $C_{10}H_{14}Cl\cdot SO_2\cdot NH_2$, crystallises from dilute alcohol in plates, and melts at 156—157°.

When the β-sulphonic chloride is heated at about 160° it is rapidly decomposed, sulphur dioxide being evolved; the main product is a colourless, very volatile, pleasant-smelling oil, but a small quantity of a crystalline substance is also obtained.

In their behaviour, when heated, these two chlorocamphenesulphonic chlorides evidently resemble the sulphonic derivatives of camphor, which, as we have recently shown, are readily converted into halogen derivatives, losing sulphur dioxide. The exact manner in which these two by-products are formed is not yet known, but it seems probable that they are produced by the action of phosphorus pentachloride on camphorsulphonic chloride.

NOTICES OF BOOKS.

The Progress of Science: its Origin, Course, Promoters, and Results. By J. Villin Marmery. With an Introduction by Samuel Laing. 8vo. London: Chapman and Hall. 1895.

In this painstaking and accurate work the Author has given us an account of the rise and development of Science from the earliest times up to the present day.

It will be obvious to all that, in dealing with so stupendous a subject within the limits of some 400 pages, this work *must* of necessity treat briefly of many important and interesting facts. On the other hand,—and that, in our opinion, greatly enhances the value of the work,—there is a copious and well-arranged Bibliography, which indicates to the Student, at a glance, where he may further pursue the study of the questions here introduced to his notice.

In these days, when we are under the thrall of "Examinationism," it is refreshing to find a book of this character which has not been compiled in accordance with any required Syllabus to meet the needs of a particular examination, but launches out on an independent track boldly and fearlessly, and at the same time honestly and straightforwardly.

The chapter which is devoted to the Progress of Science among the Arabs is one of the attractions of the book. It is pointed out that, up to now, sufficient justice has not been done to the Arabs.

Another very interesting feature is the chapter devoted to the vindication of Roger Bacon, in which the author contends that Roger Bacon was vastly the superior of Francis Bacon, and preceded the latter in the subject-matter which makes up the "Novum Organum."

Turning to the chapter on Modern Science, we find that the author has treated this difficult subject with care and judgment. Especially may we refer to the sections devoted to the weighing of the relative claims of Priestley and Lavoisier, and to the consideration of Crookes's speculation on the Genesis of the Elements.

The Index is copious and excellent.

We cordially wish the author every success in his bold venture, and we trust that the work may meet with the circulation which its merits deserve.

Essays of Jean Rey, Doctor of Medicine. On an Enquiry into the Cause wherefore Tin and Lead Increase in Weight on Calcination (1630). Crown 8vo., pp. 54. Edinburgh: W. F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co. (Ltd.). 1895.

This little work forms No. 11 of the series of the "Alembic Club Reprints." It is an interesting step towards the right understanding of the process of oxidation as established by Lavoisier a century and a half later. The author still recognises the four elements of antiquity, earth, water, air, and fire, though he contends that all matter possesses weight. At times there crops up a mention of the three chemical elements, salt, sulphur, and mercury. He shows himself versed in the principles of experimental enquiry. But he holds that water is "a simple substance beyond question." By a series of experiments he demonstrates that "it is not the disappearance of the celestial heat giving life to the lead, or the death of the latter, which augments its weight on calcination,"—a highly metaphysical, or rather unphysical, notion,—that it is not the consumption of the aërated particles which augments the weight of the lead, that the increase does not come from the vessel, that it is not due to the vapours from the charcoal, or the "volatile salt of the charcoal," or the mercurial volatile salt, or the moisture attracted by the calx; and he asks why it does not increase in weight infinitely? But he does not raise the converse question, why a given volume of air does not increase the weight of an unlimited quantity of lead or tin? Had he done this experimentally he would have trodden very closely upon the heels of Lavoisier and Priestley; but he regards air as a simple substance, saving the presence of certain possible impurities.

The perusal of this book will show us what an amount of erroneous and obscure notions had to be got rid of before the rational progress of chemistry could commence.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 14, April 8, 1895.

On the Fluted Spectrum.—H. Poincaré.—This memoir is too exclusively mathematical for transference to our pages.

Transfer of the Capital of Brazil.—H. Faye.—This startling enterprise seems to be dictated by sanitary considerations. The new capital will be placed at an altitude of 1000 metres. The climate is said to resemble that of the extreme south of France. The water supply will exceed 1000 litres per head for a population of a million, and there will be no danger of malaria.

A New Apparatus called the Comparative Hema-Spectroscope. — M. de Thierry.—This apparatus, extremely sensitive, offers every guarantee of exactitude, and may render services in forensic medicine, in biological and analytical chemistry, and in physics by the comparative study of the absorption spectra of liquids examined in a great thickness. Its construction cannot be described intelligibly without the accompanying figure.

Simple Experiment showing the Presence of Argon in Atmospheric Nitrogen.—M. Guntz.—As an absorbent for argon the author has selected lithium, which combines readily with nitrogen at a temperature below dark redness. After the introduction of a sufficient volume of atmospheric nitrogen the apparatus remains full of argon. If, on the contrary, nitrogen is introduced from the decomposition of a chemical compound nothing remains unabsorbed.

The Spectra of Selenium and of some Native Selenides.—A. de Gramont.—The author gives an elaborate table of the rays in the spectrum of selenium and of Berzeline, Cu_2Se, Zorgite, $(PbCu_2)Se$, Claisthalite, PbSe, Eucainite, Cu_2Se,Ag_2Se (from Atacama), and Guarajuatite, Bi_2Se_3.

Determination of Thiophene in Benzene. — G. Denigès.—The author places in a 60 grm. flask 20 c.c. of his mercuric reagent, HgO 50 grms., SO_4H_2 200 c.c., water 1 litre, and adds 2 c.c. of benzene. He stoppers the flask, keeps the cork in its position by means of a wire, and heats in a boiling water-bath for a quarter of an hour, agitating frequently so as to emulsify the benzene with the reagent. At the end of this time it is allowed to cool and filtered through a tared filter, washed with boiling water, and dried at 110°—115° until the weight is constant, and weighed. The increase of the weight of the filter multiplied by $\frac{84}{1108} = 0{\cdot}0758$ shows the quantity of thiophene contained in the 2 c.c. of benzene.

Action of Potassium Permanganate with various Organic Matters.—E. Maumené.—The author states that manganese peroxide has always been regarded as insoluble in water, in the majority of dilute acids, and especially in neutral media, sugar, alcohol, &c. As far as sugar is concerned this is an error.

On the Calcium Phosphate of Milk.—L. Vaudin.—The author concludes from his experiments that—1. Milk contains citric acid in the state of an alkaline citrate, which contributes to keep in solution the calcium phosphate present. 2. This solution is due to the important part played by lactose in presence of alkaline citrates. 3 All circumstances which may modify or destroy the molecular equilibrium of the salts dissolved in the milk tend to precipitate tricalcic phosphate with an excess of lime in the state of citrate.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 107.

This number contains no chemical matter.

Archives Néerlandaises des Sciences Exactes et Naturelles. Vol. xxviii., Part 5.

This issue contains no chemical matter.

MISCELLANEOUS.

Zeitschrift für Anorganische Chemie.—We are happy to announce that this valuable journal will not be suspended in consequence of the regretted death of Dr. G. Krüss, its late editor. It will be continued by Dr. Richard Lorenz, a "privat docent" of the University of Göttingen, with the co-operation of Professor W. Nernst, and will be published as before by the firm of Leopold Voss, of Hamburg. The editor, whilst retaining the characters of the *Zeitschrift*, purposes to include in addition chemical physics and electro-chemistry. It has our best wishes for its continued success.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—Society of Arts, 8. (Cantor Lectures). "Recent American Methods and Appliances employed in the Metallurgy of Copper, Lead, Gold, and Silver," by James Douglas.

TUESDAY, 30th.—Royal Institution, 3. "Alternating and Interrupted Electric Currents," by Professor George Forbes, F.R.S.

— Institute of Civil Engineers, 8.

WEDNESDAY, May 1st.—Society of Arts, 8. "Deviations of the Compass," by Prof. A. W. Reinold, F.R.S.

— Royal Institution, 5. (Annual Meeting).

THURSDAY, 2nd.—Royal, 4 30.

— Royal Institution, 3. "The Liquefaction of Gases," by Prof. Dewar, F.R.S.

— Chemical, 8.

FRIDAY, 3rd.—Royal Institution, 9. "The Structure and Function of the Horse's Foot," by Veterinary Captain Frederick Smith.

— Quekett Club, 8.

— Geologists' Association, 8.

SATURDAY, 4th.—Royal Institution, 3. "English Music and Musical Instruments of the 16th, 17th, and 18th Centuries," by Arnold Dolmetsch.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1849.

ON A

GAS SHOWING THE SPECTRUM OF HELIUM, THE REPUTED CAUSE OF D_3, ONE OF THE LINES IN THE CORONAL SPECTRUM.[*]

By WILLIAM RAMSAY, F.R.S.,
Professor of Chemistry, University College, London.

In the course of investigations on argon, some clue was sought for which would lead to the selection of one out of the almost innumerable compounds with which chemists are acquainted, with which to attempt to induce argon to combine. A paper by W. F. Hillebrand, "On the Occurrence of Nitrogen in Uraninite, &c." (*Bull. of the U. S. Geological Survey*, No. 78, p. 43), to which Mr. Miers kindly directed my attention, gave the desired clue. In spite of Hillebrand's positive proof that the gas he obtained by boiling various samples of uraninite with weak sulphuric acid was nitrogen (p. 55)—such as formation of ammonia on sparking with hydrogen, analysis of the platinochloride, vacuum-tube spectrum, &c.—I was sceptical enough to doubt that any compound of nitrogen, when boiled with acid, would yield free nitrogen. The result has justified the scepticism.

The mineral employed was clèveite, essentially a uranate of lead, containing rare earths. On boiling with weak sulphuric acid a considerable quantity of gas was evolved. It was sparked with oxygen over soda, so as to free it from nitrogen and all known gaseous bodies except argon; there was but little contraction; the nitrogen removed may well have been introduced from air during this preliminary experiment. The gas was transferred over mercury, and the oxygen absorbed by potassium pyrogallate; the gas was removed, washed with a trace of boiled water, and dried by admitting a little sulphuric acid into the tube containing it, which stood over mercury. The total amount was some 20 c.c.

Several vacuum-tubes were filled with this gas, and the spectrum was examined, the spectrum of argon being thrown simultaneously into the spectroscope. It was at once evident that a new gas was present along with argon.

Fortunately, the argon-tube was one which had been made to try whether magnesium-poles would free the argon from all traces of nitrogen. This it did; but hydrogen was evolved from the magnesium, so that its spectrum was distinctly visible. Moreover, magnesium usually contains sodium, and the D line was also visible, though faintly, in the argon-tube. The gas from clèveite also showed hydrogen lines dimly, probably through not having been filled with completely dried gas.

On comparing the two spectra, I noticed at once that while the hydrogen and argon lines in both tubes accurately coincided, a brilliant line in the yellow, in the clèveite gas, was nearly *but not quite* coincident with the sodium line D of the argon-tube.

Mr. Crookes was so kind as to measure the wave-length of this remarkably brilliant yellow line. It is 587·49 millionths of a millimetre, and is exactly coincident with the line D_3 in the solar chromosphere, attributed to the solar element which has been named *helium*.

Mr. Crookes has kindly consented to make accurate measurements of the position of the lines in this spectrum, which he will publish, and I have placed at his disposal tubes containing the gas. I shall therefore here give only a general account of the appearance of the spectrum.

While the light emittted from a Plücker's tube charged with argon is bright crimson, when a strong current is passed through it, the light from the helium-tube is brilliant golden-yellow. With a feeble current the argon-tube shows a blue-violet light, the helium-tube a steely-blue, and the yellow line is barely visible in the spectroscope. It appears to require a high temperature, therefore, to cause it to appear with full brilliancy, and it

	Argon-tube.	*Helium-tube.*	
Red	1st triplet.	1st triplet.	Equal in intensity.
	2nd pair.	2nd pair.	" "
	Faint line.	Faint line.	" "
	Stronger line.	Stronger line.	" "
	Brilliant line.	Dull line.	Weak in helium.
	Strong line.	Very dim line.	
Red-orange	Moderate line.	Moderate line.	Equal in intensity.
	" "	" "	" "
	" "	" "	" "
Orange	Faint line.	Faint line.	" "
	Triplet.	Triplet.	" "
Orange yellow ..	Pair.	Pair.	" "
Yellow	Absent.	Brilliant.	W = 587·49. (the helium line, D_3).
Green	7 lines.	7 lines.	Equal in intensity.
Green-blue	5 lines.	5 lines.	" "
	Absent.	Faint.	In helium only.
	Absent.	Brilliant.	" "
Blue	Absent.	8 lines.	" "
Blue-violet	3 lines, strong.	Barely visible, if indeed present at all.	
	2, fairly strong.	2, fairly strong.	Equal in intensity.
Violet	Absent.	Bright line.	In helium only.
	Absent.	4 bright lines.	
	Violet pair.	Violet pair.	Equal in intensity.
	Single line.	Single line.	" "
	Triplet.	Triplet.	" "
	Triplet.	Triplet.	" "
	Pair.	Pair.	" "

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[*] A Paper read before the Royal Society, April 25th, 1895.

may be supposed to be part of the high-temperature spectrum of helium.

The accompanying table gives a qualitative comparison of the spectra in the argon-[*] and in the helium-tubes.

It is to be noticed that argon is present in the helium tube, and by the use of two coils the spectra could be made of equal intensity. But there are sixteen easily visible lines present in the helium-tube only, of which one is the magnificent yellow, *and there are two red lines strong in argon and three violet lines strong in argon, but barely visible and doubtful in the helium-tube.* This would imply that atmospheric argon contains a gas absent from the argon in the helium-tube. It may be that this gas is the cause of the high density of argon, which would place its atomic weight higher than that of potassium.

It is idle to speculate on the properties of helium at such an early stage in the investigation; but I am now preparing fairly large quantities of the mixture, and hope to be able before long to give data respecting the density of the mixture, and to attempt the separation of argon from helium.

ON THE PRESENCE OF HELIUM IN CLÈVEITE.

By P. T. CLÈVE.

We have examined the gas of clèveite at the laboratory of the University of Upsala, and I judge it proper to communicate to you the result.

The mineral had been found at Carlshaus, in Norway. One of my pupils, Herr Langlet, heated a mixture of the mineral with potassium disulphate in a combustion tube. The gas, after being passed over copper at redness, was collected over a concentrated solution of potassa.

The spectrum of the gas does not display the lines of argon, as we have been able to verify by means of a tube argon which I have received from Prof. Ramsay. According to the measurements of Prof. Thalén, the rays are:—

Wave-lengths.	Atlas.	Intensities.
λ 6677	Angström.	Medium strong.
λ 5875·9	Micrometric measurement.	Strong.
λ 5048	Rowland Photog. charts.	Medium strong.
λ 5016		Strong.
λ 4922		Medium strong.
λ 4713·5	Angström.	Weaker.

The presence of helium in a terrestrial substance is therefore established. It appears probable that the strong helium line (λ 5875·9) is accompanied on each side by two very faint lines.—*Comptes Rendus*, cxx., p. 834.

OBSERVATIONS ON ARGON: FLUORESCENT SPECTRUM.

By M. BERTHELOT.

Prof. Ramsay, since his recent visit to Paris, has had the kindness to send me a second specimen of argon, amounting to 90 c.c., to subject it to further experiments. Before describing them I consider it my duty to thank him, and to invoke his guarantee for the purity of the specimens of a gas which I have not myself prepared.

These fresh experiments have referred principally to the study of the fluorescence spectrum which is observed with argon charged with vapour of benzene, and submitted to the moderate action of the effluve on certain conditions which seem to correspond to a particular state of equilibrium; for the quantity of gas absorbed does not exceed some hundredths, even after a considerable time. This limited equilibrium is analogous to that of the combination of nitrogen and hydrogen under similar circumstances.

For this purpose an observation is necessary. In fact, the two specimens of gas which have been sent me successively behaved in a slightly different manner, though giving equally signs of combination in presence of benzene. With the second the absorption was found limited to between six- and ten-hundredths of the original volume, whilst the first specimen has undergone successive absorptions which reduced it to the fifth of its original volume. This difference may correspond to particular conditions which I have not yet succeeded in defining, as I now do, for the production of fluorescence; but it may also be explained by the existence in the first specimen of a considerable proportion of nitrogen introduced by some accident in filling and sealing the tube which was sent me. To this question I purpose returning.

However it may be, these are the conditions of the fluorescence excited by the effluve:—

I operated with the assistance of a powerful Ruhmkorff's coil, fitted with a Leyden jar and a Marcel Deprez interrupter actuated by a battery or by accumulators; the length of the sparks which could be occasioned between the external wires being from 10 to 12 m.m. In several experiments I found it advantageous to interrupt one of these wires, so as to determine a flow of sparks in front of the tube submitted to the effluve; we succeed even with a sensibly greater external striking distance.

We will first explain the phenomenon in a general manner before giving measurements relating to the rays observed.

Under the above condition, at the end of a time varying from fifteen minutes to four or five hours, the silent discharges became gradually luminous, and the tube was lighted up, in almost its entire extent, at first with a violet tint with a reddish rain of fire; then the fluorescence took a lustre more and more intense, and changed gradually to a splendid green shade, visible at a distance even in full daylight, but more brilliant in darkness. With a greater striking distance the light became blue.

At this point the phenomenon remained for several hours. On stopping the current the light was at once extinguished. On re-establishing it, it at once reappeared if the stoppage had been of a brief duration; at the end of some minutes, if it had been longer the light reappeared, setting out from the point where the electric tension is greatest. Still after the lapse of a certain number of hours, especially if we increase the intensity of the discharges, the green tint is finally extinguished, leaving only a milky light which cannot be analysed by the spectroscope. All these phenomena have been reproduced from eight to ten times in different tubes; they are manifested in the gas near the atmospheric pressure, which is very characteristic.

On directing an ordinary spectroscope to the fluorescent tube we see appear a series of rays very distinct and specific,—that is to say, a yellow ray, a green ray (the most brilliant of all), and two violet rays less visible, especially the last, which is not well seen except in darkness. We see also certain rays or bands in the violet region, in the green, and especially in the red and the orange region, but I have not succeeded in defining them sufficiently for a further description. On my first experiment with the first specimen of argon I saw also a fine red ray, analogous to that of hydrogen, but it was not reproduced with the second specimen. The specific rays which I have just mentioned appeared as soon as the violet fluorescence was sufficiently established; they are very beautiful without being displaced by the green or blue fluorescence, but they become invisible when it has disappeared.

I have determined the position of these rays with a single-prism spectroscope, but unfortunately with a feeble dispersion, the experiments made with a spectroscope of

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[*] The tube then used was the one with which Mr. Crookes's measurements of the argon spectrum were made. It contains absolutely pure atmospheric argon.

great dispersive power having afforded too little light. Under these conditions we view a broad luminous surface, enlightened by a floating fluorescence, where the point of maximum illumination is continually displaced, fatiguing the eye of the observer. The divisions of the scale have been found by means of the two rays of hydrogen C and F, a ray of lithium, the D ray of sodium, and a ray of thallium projected simultaneously with the rays which I am studying.

We obtain thus several points well defined, which enable us to establish by a curve the graduation of the scale and the wave-lengths. Thus, with the aid of M. Mascart, I have determined the following numbers, which must be regarded merely as approximate, the approximation being comprised between 0·005 and 0·003, according to the part of the scale in view.

The yellow ray is very distinctly separated from the ray D, and is nearer to the green region, with an approximate value of 0·579 in place of 0·5896 (D). Still, on operating with an effluve of suitable intensity, this ray is furnished with fine black absorption lines, which indicate the possibility of its resolution.

The green ray is situate near 0·547. It is also furrowed with black lines.

The finest of the violet rays is about 0·438, and the second about 0·436.

None of these rays coincides with that of helium (0·5875), nor exactly with the principal ray of the aurora (0·557), though this last ray seems attributable to fluorescent manifestations analogous or identical, as will be said further.

They correspond, on the contrary, to the brilliant rays of the spectrum of rarefied argon contained in the tube which Prof. Ramsay has sent to the Physical Society of Paris.

The yellow ray may, in fact, be approximated to the number of 0·575, observed by Mr. Crookes, and the ray 0·578 of the aurora.

The green ray corresponds to the number 0·549, or rather to the group of Mr. Crookes, comprised between 0·555 and 0·549. Mr. Crookes's ray, 0·5557, may also be approximated to the principal ray of the aurora.

Lastly, the two violet rays correspond to the numbers 0·433 and 0·430 of Mr. Crookes; they answer also to an important ray of the aurora.

The appearance of these rays of fluorescence, at the atmospheric pressure, would seem to indicate the presence of a hydrocarbon compound of argon of the order of acetylene, or rather of hydrocyanic acid, also in a state of electric dissociation. We further remark their relations, and more generally the resemblance, which the present fluorescence and the rays of argon bear to the fluorescence and the rays of the aurora and of the zodiacal light.—*Comptes Rendus*, cxxx., p. 797.

THE PRODUCTION OF SLATY CLEAVAGE IN AMORPHOUS CELLULOSE.

By CLAYTON BEADLE.

A cellulose coagulum obtained by the spontaneous decomposition of cellulose thiocarbonate when cut in sections by a knife can be readily freed from by-products by suspending the sections in water. The sheets so obtained consist of 15 per cent of cellulose and 85 per cent of water of hydration. They are of a soft flexible nature, like rubber. We find that the dehydration can be effected by the application of high pressure, and that a compact horny sheet can be obtained by this means containing 10 per cent of atmospheric moisture. The original coagulum is homogeneous, but on the application of pressure, under certain conditions, it is found to exhibit slaty cleavage. On tearing, the edge of the film is found to consist of laminæ of uniform thickness. By varying the mode of applying the pressure and other conditions of treatment, it appears the laminæ may be made to vary in thickness. Sometimes the films are found to consist of two laminæ of equal thickness, and sometimes of a number. Films may be obtained which do not appear to exhibit this property.

It appears that when the material is dehydrated by the application of pressure, that it does not always tend to compact itself with one film, but often into laminæ, and that their thickness varies with the conditions of the pressure, &c.

In order to avoid slaty cleavage in the production of these films, it is necessary to press under conditions that would tend to give rise to laminæ of a thickness greater than that of the ultimate film obtained.

Slaty cleavage may be very much increased by passing the dry thick sheets a large number of times under high pressure between iron rollers.

4, New Court, Lincoln's Inn.

A PREDICTION OF THE DISCOVERY OF ARGON.

By C. J. REED.

The "Remarks on Atomic Weights" of argon and other hypothetical elements, by M. de Boisbaudran, translated from *Comptes Rendus* in the Chemical News, vol. lxxi., p. 116, are very interesting, not only as an evidence of his having predicted the discovery of argon, but also as an illustration of the manner in which different individuals, entirely independent of each other, arrive at the same conclusions.

While M. de Boisbaudran does not publish the reasons for his belief, nor explain the basis of his system, he states that he has found a classification of the elements that enables him to assume the existence of a family of elements, no member of which is hitherto known; that their atomic weights are 20·0945, 36·49±0·08, 84·01±0·02, and 132·71±0·85, assuming O = 16. H states further that they should be non-metallic; that the bodies 20·0945 and 36·49 should be relatively abundant in nature, the other two rare.

"The atomicity of the new family should be even, (octo-atomic), but its component elements should be devoid of the faculty of combining with other elements.

"The element 36·40 should be more volatile than sulphur, and the element 20·0946 more volatile than oxygen. Lastly the elements 84·01 and 132·71 should be respectively more volatile than selenium and tellurium."

About ten years ago the writer devised a classification of the elements based solely on the numerical relations between valence and atomic weight.

This classification was described by me in a paper read before the American Association for the Advancement of Science in August, 1885; and in a more complete paper on the "Graphical Representation of the Relation between Valence and Atomic Weight," read before the St. Louis Academy of Science a few weeks later (*Trans. St. Louis Academy of Science*, iv., No. 4).

Plate I. and Figs. 3 and 4 of that paper are reproduced here in fac simile.

In this classification the elements were arranged by locating a point in a plane for each element by rectangular co-ordinates, taking ordinates proportional to the valence, and abscissæ proportional to the atomic weight.

It was found that the loci of two equations, $y = a(x-4)$ and $y = a(x-5)$, pass through or near the points corresponding to more than fifty of the elements whose physical constants are most accurately known; provided the plane is wrapped around a cylinder having its axis parallel with the axis of abscissæ and its radius,—

$$R = \frac{8a}{\pi}.$$

The loci of these equations now become parallel helixes that cut the axis of abscissæ at intervals of sixteen units of atomic weight. The ordinates become arcs of circles formed by planes cutting the cylinder at right-angles to its axis. The axis of abscissæ becomes an element of the surface of the cylinder. The circumference of the cylinder measures eight units of valence. Valence is measured upward from the axis of abscissæ if it is electro-positive, and downwards if it is electro-negative. Elements that exhibit both electro-positive and electro-negative valence (such as chlorine, bromine, iodine, sulphur, selenium, tellurium, nitrogen, phosphorus, carbon, and silicon) show a difference of eight units of valence between the highest electro-positive and the lowest electro-negative values. The locus $y=a(x-4)$ seems to contain mostly artiads, and the locus $y=a(x-5)$

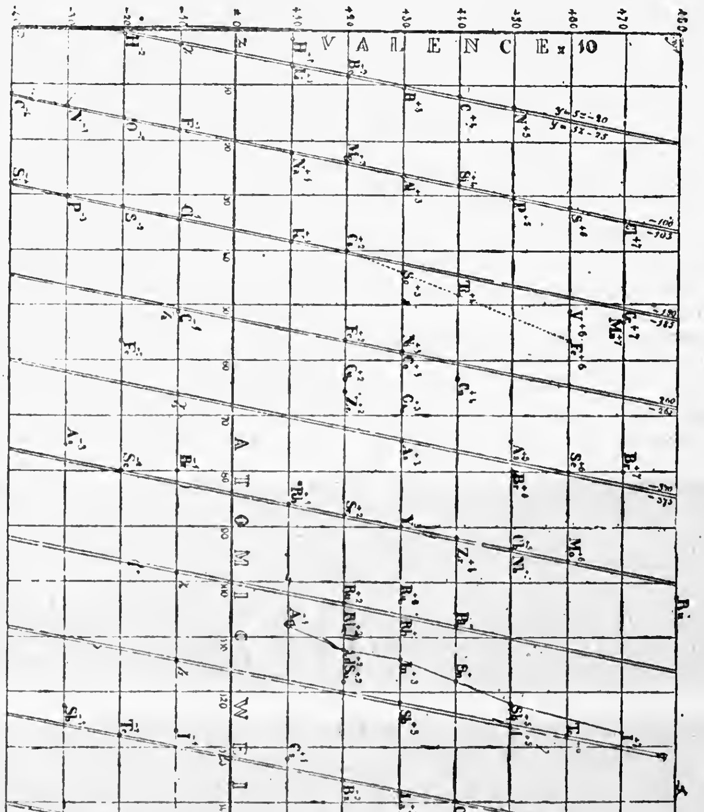

PLATE I. Showing the Relation between Valence and Atomic Weight.

mostly perissads. The complete development of the system would necessitate the existence of four groups or families of artiad elements and four groups of perissads. One of the artiad groups would be a group of undiscovered elements having the following peculiar properties:—

1. The most marked valences of these elements should be either zero or eight; that is, these elements should either combine as octads or else be incapable or nearly incapable of combining with other elements.

2. The total possible number of these elements is fifteen. Their atomic weights are 4, 20, 36, 52, 68, 84, 100, 116, 132, 148, 164, 180, 196, 212, and 228.

3. The only elements of this group that are likely to be found in nature are 4, 20, 36, 84, 132, and 196, possibly 180.

4. The elements of this group should all be highly volatile and probably mon-atomic.

5. Elements 4, 20, and 36 should be comparatively abundant in nature, like most elements of low atomic weight, and they should be non-metallic.

6. Elements 84 and 132 should be comparatively scarce, but not more rare than selenium or tellurium. They should form explosive compounds with oxygen or chlorine.

7. Element 196 should be a metal, heavier and scarcer than gold, and capable of easier reduction to the metallic state; also capable of forming an oxide having the formula RO_4, or alkaline salts having the formula K_2RO_5. The volatile metal osmium agrees very closely with the requirements of this element; while ruthenium may possibly be the element 100.

8. Elements of this group will not combine with one another, and those having low atomic weights will probably not combine with any element, except possibly to form highly explosive compounds with one or two elements. Such compounds could exist only at very low temperatures.

9. Element 20 should bear to element 36 a relation like that of fluorine to chlorine or that of oxygen to sulphur; also 84 should bear to 132 a relation like that of bromine to iodine or that of selenium to tellurium.

The necessity for these elements impressed me very strongly at that time; but I had not the temerity to believe, for the sake of completing my classification, that there could really exist so large a group of elements, all of them entirely unknown, and having such remarkable properties as that of being unable to combine with other elements.

I was content, therefore, to believe this to be a defect in my classification and to merely mark the position of the two most necessary elements on my charts, without indicating that they stood for unknown elements. In Figs. 3 and 4 their positions are indicated at the points marked ± 0. The one in Fig. 3, between fluorine and sodium having the atomic weight 20, and the one in Fig. 4 between chlorine and potassium having the atomic weight 36.

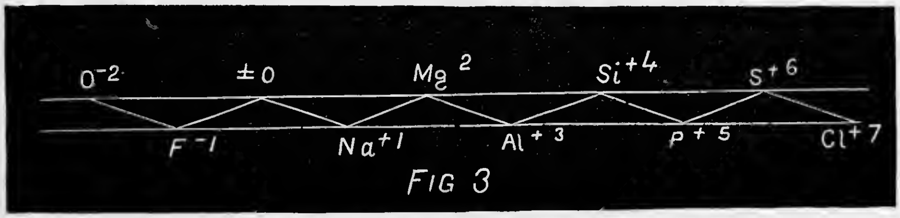

Fig 3

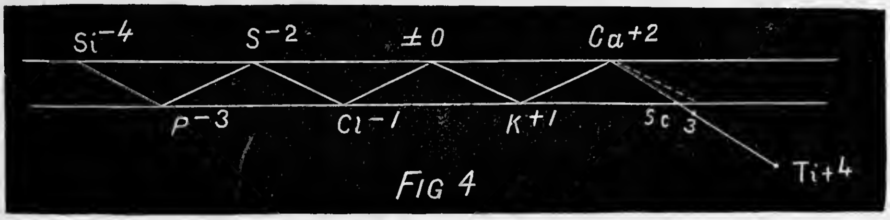

Fig 4

I have no desire to claim a post-mortem prediction of argon, but merely to show that I published ten years ago a classification of the elements on which all of M. de Boisbaudran's deductions might have been predicated.

ON THE

ACTION OF ACETIC AND HYDROCHLORIC ACIDS ON SUCROSE.*

By H. A. WEBER and WILLIAM McPHERSON.

While carrying out some experiments with glucose several facts were noticed in reference to the action of acetic and hydrochloric acids on sucrose, which it is interesting to compare with the conclusions reached by Bornträger (*Boh. Zeit. Zucker, Ind.*, 1891, 187; *Bull. Assoc. Chim.*, 1892, 559), Jungfleisch and Grimbert (*Compt. Rend.*, cvii., 390, and cviii., 144), and Ost (*Ber. d. Chem. Ges.*, xxiv.. 1636). Inasmuch as we were working with an entirely different object in view, the conclusions reached were in no way influenced by the conclusions reached by the above writers.

While making an examination of a large number of saccharine products, the writers were led to believe from certain results that complete inversion could be effected by means of acetic acid. This view was contrary to the general opinion of chemists, although as prominent ones as Jungfleisch and Grimbert (*Compt. Rend.*, cvii., 390) claim that acetic acid completely inverts sucrose at 100°, and that it is preferable to other acids, since its presence is without effect upon the levulose of invert sugar. This conclusion was reached from the fact that the specific rotatory power of pure levulose corresponded almost exactly with that of levulose calculated from invert sugar, the inversion being effected by acetic acid. Hydrochloric acid gives a higher invert reading, because, in some way, it acts upon the levulose and increases very perceptibly its specific rotatory power. Exceptions to this view are taken by Maumené (*Journal des Fabricants du Sucre*,—Abstract from March 27th, 1889), who calls attention to the fact that the invert sugar prepared from sucrose by action of acids is not composed of equal parts of levulose

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* *Journal of the American Chemical Society*, vol. xvii., No. 4, April, 1895.

and dextrose. Ost (*Ber. d. Chem. Ges.*, xxiv., 1636) not only denies that acetic acid will produce complete inversion, but also claims that it acts perceptibly upon invert sugar. Ross ("Report of the Association of Official Agricultural Chemists," Bul. 35, Div. of Chem., Dept. Agr., p. 146) states, as the result of a number of experiments, that it was found impossible to secure complete inversion even when 10 per cent glacial acid was used and the flask kept immersed in boiling water for forty-five minutes.

Those who claim that acetic acid does not effect complete inversion base their belief upon the fact that invert sugar, prepared by the action of hydrochloric acid upon sucrose, gives a higher reading than the corresponding solution obtained by the action of acetic acid. It was thought that perhaps acetic acid might form some compound with the constituents of the invert sugar, which might affect the reading of the polariscope. Proceeding upon this assumption, attempts were made to decompose such a compound. In the course of these experiments, which were conducted at great length, certain facts were noted which have been systematised in the following:—

As stated above, Jungfleisch and Grimbert in particular have called attention to the fact that the specific rotatory power of invert sugar, prepared by the action of hydrochloric acid on sucrose, is higher than that of the artificially-made invert sugar. If, however, as Maumené claims, the invert sugar so prepared is not composed of equal parts of dextrose and levulose, then it is possible that the different readings are due to the peculiar compounds formed. In fact one would not expect the readings to be identical under such assumptions.

Accordingly experiments were undertaken to find out, if possible, whether the hydrochloric acid used in inversion affected in any way by its presence the reading of the invert sugar so prepared. Attempts were made in two different directions.

1. Five hundred c.c. of a normal solution of sucrose (polarising at 99·8) was subjected to inversion in 100 c.c. flasks by adding one-tenth the volume of concentrated hydrochloric acid (sp. gr. 1·19) and heating for ten minutes, regulating the heat so that the temperature, 68°, was reached at the end of that time. These solutions were all poured into a large flask and thoroughly mixed, so as to obtain a perfectly uniform solution. Exactly 55 c.c. of this solution were transferred to a 100—110 c.c. flask, the flask filled to the mark with water, the solution thoroughly mixed and polarised. The experiment was repeated with the addition of 5 c.c. of the same acid used in the inversion, previous to filling to the mark with water; again repeated with the addition of 10 c.c., 15 c.c., and 20 c.c., respectively. Since the same solutions, same flasks, and polarising tubes were used, and the temperature of the solutions did not differ more than 0·5°, corrections being introduced for this variation, the chances of error in manipulation were very slight. The following readings, expressed in divisions of cane-sugar scale, were obtained for the various solutions (temperature = 20°):—

Invert sugar (containing 5 c.c. of acid)..	−33·00
Invert sugar + 5 c.c. additional acid ..	−33·90
Invert sugar + 10 c.c. additional acid ..	−34·65
Invert sugar + 15 c.c. additional acid ..	−35·60
Invert sugar + 20 c.c. additional acid ..	−36·40

The reading is seen to increase with the addition of the acid, thus agreeing with the conclusion of Gubbe (*Ber. d. Chem. Ges.*, xviii., 2207). Moreover, the deviations caused by the addition of the different amounts of acid are fairly constant, varying from 0·75 to 0·95, or an average of 0·85. It was hoped that sufficiently uniform results could be obtained to allow the graphic representation, so that an estimate could be made on the effect of the original 5 c.c. of added acid to bring about inversion. Since, however, the addition of a second, third, fourth, and fifth 5 c.c. of acid each increases the reading of the invert sugar approximately 0·85, then we may conclude, with some probability, that the original 5 c.c. of acid which effected the inversion would increase the reading by that amount.

2. Attempts were also made to solve the problem by neutralising the acid present in the invert solution by the action of sodium carbonate.

Bornträger (*Boh. Zeit. Zucker Ind.*, 1891, 187) has called attention to the fact that the rotatory power of the neutralised solution is higher than that of the corresponding acid solutions. By the addition of sodium carbonate, however, not only is the acid neutralised, but a corresponding amount of sodium chloride is thereby added. Readings were taken first to find out the effect of the addition of the sodium chloride. Then, by comparing this with the variation caused by neutralisation with sodium carbonate, the effect of the acid could be deduced.

Five hundred c.c. of inverted sugar solution were prepared as described above. It was found that $3\frac{3}{10}$ grms. of pure dry sodium carbonate were necessary to neutralise the acid (5 c.c.) present in 55 c.c. of this solution. The experiments were conducted as in the above: 55 c.c. of the solution were transferred to a (100—110) flask, neutralised with sodium carbonate, the flask filled to the mark, the solution mixed thoroughly and polarised. The duplicates agreed within the limit of error in reading. The average readings on cane-sugar scale were as follows (temperature = 20°):—

	Triplicates.		
	1.	2.	3.
Original solution	−33·1	−33·0	−33·20
Original solution + 3·3 grms. sodium carbonate (neutral)..	−33·7	−33·7	−33·85
Original solution + 6·6 grms. sodium carbonate..	−36·2	−36·0	−36·30

The last reading was taken in order to compare the effects of the addition of sodium carbonate before and after neutralisation. It is thus seen that, while the reading of the normal solution is increased 0·6° by the addition of the necessary amount of carbonate to neutralise the acid, the subsequent addition of a like amount increases the reading 2·5°. Before ascribing this difference in reading to the effect of the acid, it is necessary to find whether or not the sodium chloride, formed by the addition of the sodium carbonate to hydrochloric acid, affected the reading.

Experiments were conducted with the same solution used above: 55 c.c. of the solution were introduced into the 100—110 c.c. flask, and the amount of sodium chloride corresponding to $3\frac{3}{10}$ grms. of sodium carbonate, or 3·65, added, the flask filled, and the solution polarised as before. The average readings on cane-sugar scale, agreeing within 0·1°, are:—

Original solution	−33·1	−33·15
Original solution + 3·65 grms. sodium chloride	−35·1	−35·10

Since, then, the effect of the sodium chloride was to increase the reading 2°, the acid remaining unneutralised, while the reading was only increased 0·6° by the addition of the same amount of sodium chloride, the acid being neutralised at the same time, the difference 1·4° may presumably be attributed to the action of the acid present.

This result is higher than the one deduced from the direct addition of acid given above, but it is undoubtedly the more correct of the two. It would thus seem that the acid undoubtedly increases the rotatory power, the probable increase of reading being about 1·4° on the direct scale for the normal solution.

Similar experiments were next conducted in order to find out the effect of acetic acid. The strength of the acid used may be inferred from the fact that 5 c.c. of it required for neutralisation 3·05 grms. of dry sodium carbonate. The normal solution of sucrose was heated at 100° with one-tenth volume of this acid for about one hour, experiments showing that continued heating had but little effect upon the reading. By this treatment a reading for the normal solution was obtained on an average of 2° lower than when hydrochloric acid was used as the agent of inversion. The same solution which gave a reading of −33·1° when hydrochloric acid was used gave a reading of −31·1 when treated with acetic acid under the above conditions.

Experiments performed to discover whether the subsequent addition of acetic acid would affect the reading, gave the following results, on cane-sugar scale:—

Original invert solution (temperature 20)	−31·10	−31·0
Original invert solution + 10 c.c. additional acetic acid	−30·85	−30·8

The second reading is the reading obtained from a solution exactly the same as the first 10 c.c. of acetic acid being introduced.

It thus appears that while hydrochloric acid increases the reading by its presence, acetic acid increases it by a small but perceptible amount. This result agrees with Ost, who criticises the statement of Jungfleisch and Grimbert that acetic acid has no effect upon invert sugar. In order to test this further, the acid was neutralised by sodium carbonate and the difference of reading noted. This result, united with the effect due to the introduction of the sodium acetate formed, gave the means of finding the effect of the acid.

The experiments were conducted as in the above, using same solution, same flask, and same polarising tubes. The following are the results obtained, on cane sugar on scale:—

Original solution (temperature 20°) ..	−31·20	−31·1
Original solution + 3·05 grms. sodium carbonate (neutral)	−32·65	−32·6
Original solution + (3·05 × 2) grms. sodium carbonate	−34·80	−34·8

A marked difference is noted here as compared with similar experiments with hydrochloric acid. The neutralisation of the hydrochloric acid increased the reading only 0·6°, while the neutralisation of the acetic acid increased the reading over twice the amount, or 1·5°. The subsequent effects of the sodium carbonate upon the two solutions agree very well, being an increase of 2·5 in the case of hydrochloric acid against an increase of 2·2° in the case of acetic acid. This difference of 0·3° in the reading is accounted for by the fact that 3·3 grms. of sodium carbonate were added in the hydrochloric acid solution, while only 3·05 grms. were added in the acetic acid solution. If correction be made for this difference, the increase in readings differ only by 0·1°.

It was necessary also to find out the effect of the sodium acetate formed by the neutralisation of the acetic acid by sodium carbonate. The readings on the cane-sugar scale were as follows:—

Original solution (temperature 20°) ..	−31·1	−31·1
Original solution + 4·72 grms. sodium acetate	−32·4	−32·4

The sodium acetate used was the pure anhydrous salt.

It is thus seen that while the sodium carbonate increased the reading 1·5°, the introduction into the original solution of the same amount of sodium acetate as was formed increased the reading but 1·3°. The difference of 0·2° must be due to the presence of the acid.

The conclusion that the acetic acid by its presence lowers slightly the reading is confirmed by the fact that by the use of a weaker acid a maximum reading of −31·3° was obtained.

As might be expected, the introduction of hydrochloric acid into a solution inverted by acetic acid increases the reading in a corresponding degree.

It is thus shown that the effect of hydrochloric acid upon a solution of invert sugar is to increase the reading, while acetic acid has an opposite effect. Moreover, the experiments show that the probable increase in reading due to hydrochloric acid under the conditions mentioned is 1·4°, while the probable decrease in reading due to acetic acid is 0·2°. In other words, if these two acids produced the same effects upon being heated with sucrose, there would still be a difference of reading of 1·6° due to the presence of the acid. This agrees fairly well with the actual difference observed.

In the light of these experiments, it may be of interest to notice the question so often discussed, "Does acetic acid effect complete inversion?" If we suppose that no acid effects complete inversion unless it gives a reading such as that obtained by using hydrochloric acid, then most certainly acetic acid does not invert completely. If, on the other hand, we adopt as the reading of the invert solution the reading of the acid solution, corrected for the effect produced by the presence of the acid, then acetic acid gives more nearly the correct invert reading, and it is correct to affirm that acetic acid does invert sucrose completely.

Finally, the above results indicated that when Fehling's solution is used in the place of the polariscope, it would be a matter of indifference whether acetic or hydrochloric acid was used to effect the inversion of the sucrose. Experiments showed this to be true. Two solutions containing the same amount of sucrose were inverted with hydrochloric and acetic acids respectively. After inversion exactly 11·7 c.c. of each solution were required to reduce 10 c.c. of Fehling's solution. Moreover, when Fehling's solution is used for the determination of sucrose in presence of dextrin or commercial glucose, acetic acid is preferable to hydrochloric acid as the agent of inversion, since the process requires no attention, and the error introduced by the hydrolysis of dextrin is less even when the most favourable method of inversion is used, viz., heating for ten minutes, regulating the temperature so as to reach 68° at the expiration of that time.

ARRANGEMENT FOR MEASURING OUT LIQUIDS.

By F. F. SKINNER,
With the Cochrane Chemical Co., Boston, U.S.A.

Whenever it becomes necessary to measure out a given volume of liquid with a pipette, and the same operation is to be repeated a number of times in succession, and the liquid to be measured is volatile and offensive, like gas-liquor, strong ammonia, hydrochloric and nitric acid, &c., more or less of the vapours are thrown into the mouth, causing at least an unpleasant taste, to say nothing about the possibility of getting the liquid itself into the mouth, with consequent risk to comfort and health.

The following arrangement is intended to remedy these objections:—

The pipette is, by means of rubber tubing, connected with a glass Y-tube, one limb of which, A, Fig. 1, is in communication with the filter-pump, or, when this is not convenient, with an aspirator bottle placed on a high shelf near by. Over the other limb, B, of the Y-tube is slipped a short piece of rubber tubing, and, like A, is closed by a glass drop as indicated in Fig. 2. Place the vessel containing the liquid to be measured under the pipette in such a manner that the latter dips under the liquid; now squeeze the glass drop at A, and the liquid will rise in consequence of the suction of the filter pump or aspirator; when it has reached the mark, which is easily done in one operation with a little practice, or is a little above it, the drop is released, and adjustment to the mark is made by cautiously squeezing the drop at B. This done, remove the vessel containing the liquid, and place under the pipette the vessel intended to receive the measured liquid; then squeeze the drop at B until the required amount of liquid has run out. The pipette is easily rinsed out, when necessary, by repeating the operation once or twice before measuring out.

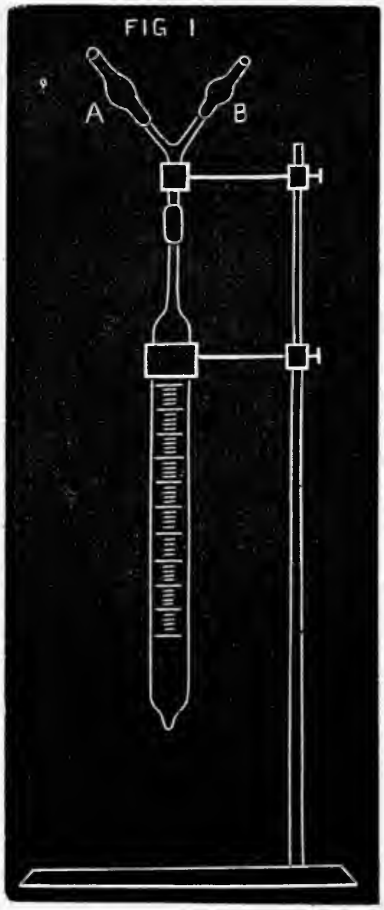
FIG 1


FIG 2

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Anniversary Meeting, March 27th, 1895.

Dr. Armstrong, President, in the Chair.

The President, in opening his Address, referred to the fact that its delivery marked the close of an official connection with the Society maintained during twenty years —a period of great activity in the history of the Society, during which the number of Fellows had increased from 800 to nearly 2000.

The first subject considered was the Faraday lectureship, which he remarked had been described as "an institution that in its most characteristic features is without parallel elsewhere," by Professor Odling, who, moreover, had said, "that having regard to the great name with which it is associated, we cannot doubt that the nomination to this lectureship will ever be held in high esteem." This very fact made the appointment one which occasions great perplexity. Having failed to induce Professor Emil Fischer to deliver the lecture, the Council had been led to fully discuss the matter and to arrive at the conclusion that it would be desirable to break through the practice originally initiated by the Council, and hitherto adhered to, of inviting only foreigners to deliver the lecture. Since this decision was arrived at, circumstances had arisen which had led to an even more novel departure. All were aware that Lord Rayleigh and Professor Ramsay had recently successfully effected the separation of a hitherto unrecognised constituent from the atmosphere, a discovery which was justly regarded as one of the most remarkable ever made in chemistry—but this was no chance discovery. On the contrary, it was the outcome of labours carried out with unwearied perseverance and patience and with consummate skill by Lord Rayleigh during many years past. After tracing the history of the discovery, the President proceeded to say that no chemist could fail to be impressed by Lord Rayleigh's work. Recognising its extreme value, the Council had decided to appoint Lord Rayleigh Faraday lecturer, and to request his acceptance of the medal in recognition of the important service which he had rendered to chemical science by his discovery of argon. They did not ask that he should give a lecture, but made the award of the medal in this special manner in order to mark their sense of the value of his labours, and especially of the example he had set. There was, however, reason to hope that Lord Rayleigh will be prepared to address the Society on the subject of argon.

The President then presented the Faraday Medal to Lord Rayleigh "in recognition of the services he had rendered to chemical science by the discovery of Argon."

Lord Rayleigh said that, in returning his thanks to the Society, he was somewhat embarrassed, because he felt that there ought to be another standing at his side. It was true that his researches, to which the President had referred, upon the densities of gases had rendered it almost certain that a new gas of some sort was concerned, and probable that the new gas was in the atmosphere. But from this point to the isolation and examination of argon was a long step, and the credit for it must be shared equally between Professor Ramsay and himself. In some quarters there had been a tendency to represent that antagonism existed between chemists and physicists in the matter, though such a thought never entered his mind. Professor Ramsay was a chemist by profession, while he himself had dabbled in chemistry from an early age, and had followed its development with a keen interest.

Being called on by the President, Professor Ramsay made a communication of the discovery of helium in clèveite. (See Chemical News, vol. lxxi., p. 151).

Mr. Crookes then gave an account of the spectrum of the gas from clèveite. (See Chemical News, vol. lxxi., p. 151).

Continuing his Address, the President said that the Society had lost an old and faithful servant in the collector, Mr. Hall, who last summer retired on a pension from the Society after being twenty-five years in its employ.

The opportunity had been taken to institute changes in the paid staff of the Society which had long been advocated by the officers but postponed mainly on financial grounds. A collector being no longer necessary, it had been decided to appoint an Assistant-Secretary, who should also act as assistant to the Treasurer and as Librarian. They had been successful in securing the services of Mr. Robert Steele, formerly a science master at the Bedford Modern School.

The fusion of the offices of Assistant-Secretary and of Librarian, effected with the object of securing the constant attendance of the Librarian, had led to the termination of Dr. Thorne's official connection with the Society; on behalf of the Council, he desired to express the warmest thanks to Dr. Thorne for the assistance he had rendered as Librarian since the death of Mr. Watts.

The numerical strength of the Society was as follows* :—

Number of Fellows, March 31, 1894		1962
" " since admitted		118
		2080
Removed on account of non-payment of four annual subscriptions	24	
Do. three annual subscriptions	33	
Withdrawn	27	
Deaths	17	
		101
Number of Fellows, March 31, 1895		1979
Foreign Members		30

These statistics were by no means satisfactory. Not only was the number admitted smaller than usual, one reason being that 23 who had been elected had failed to satisfy the conditions on which admission into the Society was granted, but an unusually large number had declined to comply with the By-laws and the Treasurer's just demands, and, therefore, were removed from the register. (The names of those who have thus, of their own act, ceased to be Fellows of the Society were then given).

The Society was fortunate in having been deprived of only seventeen of its Fellows by death, viz. :—Ashwell, J. R.; Barratt, Alex.; Beauchamp, Maj.; Board, G.; Carteighe, J.; Dunne, B. L.; Gill, C. H.; *Hughes, F. R.; Johnson, F. R.; Morris, J. E.; Nason, Prof. H. B.; Salet, G.; Twining, A. H.; White, A; Wright, C. A.; Evans, N.; Thornthwaite, W. H.

This list contains the name of one of the original Fellows of the Society, F. R. Hughes, so that now but one remains—Lord Playfair. The decease of Dr. Alder Wright at so early an age was especially to be regretted.

Three foreign members had died during the year—Marignac, v. Helmholtz, and Josiah P. Cooke. Prof. Clève had undertaken to commemorate the work of the first of these, and especially to discuss the present state of our knowledge of the chemistry of the rare earths, a subject to which Marignac devoted particular attention. Prof. Fitzgerald, F.R.S., in like manner had consented to deal with that part of the work of v Helmholtz which was of interest to chemists, viz., electrolysis and the theory of vortex atoms.

Reference was made to a somewhat virulent outbreak of the black-balling mania which affected one of the elections. Having made special enquiries with reference to those who were rejected, he was satisfied, said the President, that they were, in the majority of cases, the victims of unjust prejudice.

The Assistant-Secretary was engaged in verifying the register of Fellows, and, as illustrating the difficulties, it might be mentioned that no fewer than ninety-eight Life Fellows had not responded to the request for their present addresses.

The number of communications made to the Society during the year was 132.

Eighty-three papers were published in the *Transactions* for 1894, occupying 1039 pages; whereas in the preceding year 104 papers were published, occupying 1432 pages.

The Index to the *Transactions*, *Proceedings*, and *Abstracts* occupies 149 pages, and contains upwards of 11,000 entries.

Referring to the labours of the Editors in connection with the *Transactions* and *Abstracts*, the President said that not only the Council but all the Fellows must very fully recognise the great value of the work which is done for the Society by both gentlemen.

Taking into consideration the increase in the size of the *Journal* and its great value, the Council had resolved to increase the sale price to 40 shillings per annum after this year.

Among other topics, reference was made to the issue of abstracts of physical papers by the Physical Society; also to the federation of the various Brewing Institutes, and the issue by them of a Journal, which, besides original matter, was to contain abstracts of papers of special interest to those engaged in the brewing industry.

The technical portion of the address dealing with the ionic dissociation hypothesis and the correlation of structure with function, among other matters, having been taken as read,—

Sir Frederick Abel proposed a vote of thanks to the President, coupled with the request that he allow his Address to be printed. Dr. W. H. Perkin seconded the motion, which was carried by acclamation. The President having thanked the meeting,—

Professor Thorpe, the Treasurer, gave an account of the Balance Sheet, which he laid before the Society, duly audited.

Scrutators were appointed, and a ballot was then taken for the election of officers and Council for the ensuing year; the following were subsequently declared elected :—

President—A. Vernon Harcourt, M.A., LL.D., D.C.L., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, LL.D., Ph.D., F.R.S.; A. Crum Brown, D.Sc., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L, F.R.S.; Sir 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, LL.D., Ph.D., F.R.S.; Lord Playfair, K.C.B., Ph.D., 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.; Horace T. Brown, F.R.S.; F. R. Japp, M.A., Ph.D., LL.D., F.R.S.; Ludwig Mond, F.R.S.; C. O. Sullivan, F.R.S.; W. C. Roberts-Austen, C.B., F.R.S.

Secretaries — J. M. Thomson; W. R. Dunstan, M.A., F.R.S.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—T. E. Thorpe, LL.D., F.R.S.

Other Members of Council—P. P. Bedson, D.Sc.; B. H. Brough; H. B. Dixon, F.R.S.; Bernard Dyer, D.Sc.; R. J. Friswell; O. Hehner; F. S. Kipping, Ph.D., D.Sc.; H. McLeod, F.R.S.; W. A. Shenstone; T. Stevenson, M.D.; W. P. Wynne, D.Sc.; S. Young, D.Sc., F.R.S.

NOTICES OF BOOKS.

The Analysis of Beers, Spirits, and Vinegar. A Guide to Decisions and Opinions on Beers, Spirituous Drinks, Liqueurs, Arrac, Rum, Cognac, and Vinegar. (Die Analyse der Biere, Spirituosen, und des Essigs. Leitfaden zur Beurtheilung und Begutachtung von Bieren, Spirituosen — Brantweinen, Likören, Arrak, Rum, Kognac — und Essig). Compiled by H. A. Blücher, Sworn Chemist and Judicial Expert. With 25 Woodcuts in the Text. Crown 8vo., pp. 291. Kassel: Brunnenmann.

This work is the second volume of a series of analytical pocket-books giving indications for an exhaustive examination or a decision on important products which enter into human diet.

The author, H. A. Blücher, belongs to a class of analysts who have no representatives in Britain, that is the "vereideten chemiker," *i.e.*, scientific chemists sworn to give accurate decisions and reports on any question submitted to them by the Court. They are, we believe, not "called" by either of the litigants, but are rather the scientific assessors of the Bench.

The present volume is a concise but thorough-going manual. The introductory part speaks of the manufac-

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* This statement has been corrected to March 31, 1895.

ture of beer, its defects and diseases, and its preservation. The analytical part deals, firstly, with the raw materials, water, barley, malt, hops, wort, and yeast.

The author, like German authorities in general, considers soft waters, free from organic matter, preferable for brewing purposes, though he admits that gypsiferous waters may expedite the clearing of worts.

Next follow general and special methods for the analysis of beer. The author then shows the general principles to be kept in view in official reports on malt-liquors, with especial reference to substances which may be possibly present, but which are to be at once condemned. Such are boric and salicylic acids. It is curiously remarked that though salycilic acid must be objected to in beers for German consumption, it is admissible in such as are destined for exportation. The maximum limit for glycerin in beer is stated as 0·25 grm. in 100 grms.

Spirituous liquors are classified as spirits for ordinary consumption, such as grain- and potato-whiskey, gin, and inferior brandy. A higher grade includes arraek, rum, and cognac. The first-mentioned of these spirituous liquors contains 48 to 54 per cent by weight of alcohol; in rum the proportion reaches 65 to 73; and in cognac 40 to upwards of 60.

Among the substances which justify a condemnatory decision, aloes and gamboge find a deserved place.

The composition of absinthe is given, but there is not a word of condemnation or of caution concerning this most objectionable of all alcoholic liquors. It is remarkable that the "Temperance" party in Britain, active and watchful as they are, have never made any protest against its importation or sale in these realms.

It is stated, doubtfully, that methylic alcohol may be found in arrack and rum. Formic acid is also a questionable ingredient.

Grain- and potato-spirits are to be distinguished by their odour; 20 c.c. of the sample are mixed with 0·2 potassium hydrate, dissolved in a drop, well shaken up, and slowly evaporated to 6 grms. This residue is then shaken up in a closed test-tube, with an equal volume of dilute sulphuric acid. On opening the tube the characteristic fusel smell of grain-spirit, or the disgusting odour of potato-spirit, may be plainly recognised and distinguished.

This work will prove very useful to manufacturers of and dealers in alcoholic liquors, and still more to public analysts.

A Primer of Evolution. By Edward Clodd, President of the Folk Lore Society. With Illustrations. 12mo., pp. 186. London and New York: Longmans, Green, and Co. 1895.

This is a popular exposition of the process commonly known as evolution, but named by the French, less elegantly though perhaps more correctly, "transformism."

This transformation is traced out in the phenomena of astronomy, of geology, and of biology, vegetable and animal. The great question of chemical evolution, of the formation of our present elements from some possibly antecedent state or states, is not distinctly touched. This deficiency deprives the work, for us, of its main value. We should have been happy to see the author's views on this capital phase of the question. Perhaps Mr. Clodd might have met with some decisive evidence for or against chemical evolution.

The author seems to accept the Darwin-Wallace hypothesis of Natural Selection as the main, if not the sole, agency which has been brought to bear. He seems to disregard the fact that this hypothesis is certainly not gaining ground in the opinion of the scientific world. Nor does he, as far as we can perceive, remind his readers that change is not the universal law of the universe, and that where traced it may be, and often is, in the direction of degradation. This truth might, we submit, have been enforced with the more advantage as the author includes human society in the circle of his speculations, where transformation assumes a phase not of differentiation, but of a movement in the opposite direction.

Agricultural Journal. Published by the Department of Agriculture of the Cape Colony. Vol. viii., No. 5.

This issue contains not a few interesting facts and suggestions.

There prevails in Namaqualand the disgraceful superstition that it is sacrilegious to kill locusts, since they are sacred insects! We doubt if any native race in India could surpass this folly.

Canary seed (*Phalaris canariensis*) is recommended as a useful crop for cottagers; it is well suited to the climates of Africa and Australia.

The preservation of potatoes is found practicable by the Schribau process. The tubers are immersed for twelve hours in a 2 per cent solution of sulphuric acid, and then dried.

The world's stock of sheep is given as 583,030,200 head. Of these, there are in the United Kingdom, 33,642,000; Australia, 124 845,600; South Africa, 35,759,935; and Asia (chiefly India), 53,401,579. In the La Plata countries there are more than 135,000,000.

The contagious American peach-disease, the yellows, does not exist in Africa. Irrigation should never be applied by means of water left round the stem of the tree.

A process has been discovered by means of which the fruit of the loquat may be rendered seedless. It is suggested that the peach, nectarine, and apricot might be improved in a similar manner.

Bee-owners in various parts of the colony are greatly exercised by the ravages of the "bee-pirate,"—a *Philanthus* near of kin to the *Philanthus apivorus* of Europe. Here is scope for inventors!

The Most-frequently Used Apparatus and Utensils for Chemical Laboratories. Drs. Peters and Rost, Manufacturers of Chemical Apparatus and Utensils, No. 27, Sophie Charlotten Strasse, Charlottenburg, near Berlin. London Agency: Imperial Wharf, 46, Bankside, S.E.

Among the novel specialities here mentioned and figured is a shaking arrangement which has not only a lateral but a rotatory movement, and requires but little power; a diazotising funnel; a dyeing apparatus and a yarn-dyeing appliance, both for testing purposes. There is also a patent cork-squeezer for laboratory purposes, which presses and rolls the cork at the same time.

The firm also offer for sale collections of fluorescent solutions, of micro-chemical reagents, preparations for microscopic study of alkaloids, of coal-tar dye-wares, physiological chemicals, vegetable drugs, &c., for biological and chemical demonstrations.

CORRESPONDENCE.

ON THE DIMINISHING OF PIPING IN CRUCIBLE-STEEL INGOTS CAST FOR TOOL MANUFACTURE.

To the Editor of the Chemical News.

Sir,—I thank you very much for inserting the note on my system of casting and forging ingots, which seems to me by experiment to be simple and effective. My system, in fact, turns the ingot from an upright position, as now made, to a horizontal position; and, besides, the section of the ingot, 9 in. × 9 in. is much bigger than are the ingots ordinarily, 4 in. × 4 in., the height of the ingots being respectively—H, 3½ in. in my system; H, 16 in. in high ingots. The weight of the metal in both cases is about ⅔ cwt. (the charge of my crucible). In the ordinary way we obtain a funnel with a long tube (the pipe), whereas in my system the pipe is cup-formed.

There is a mistake in the dimensions of the mould as given; instead of 6 in. × 6 in. (the dimension given in the design with the walls of the mould), it must be 9 in. × 9 in. (the dimension of the mould inside), and instead 9 in. the height 6 in., counting the place for the lid (2 in. thick). The resulting ingot, roughly speaking, is 9 in. × 9 in.; height 3½ in.; = ⅔ cwt. of steel.

In a hurry one is liable to make mistakes, and I feel that I am to blame for this. Will you kindly publish this letter as a correction.—I am, &c.,

Sergius Kern.

House 2, Lodge 36.
Leshtoukoff Pereoulok,
St. Petersburg, April 11, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 15, April 16, 1895.

Observations on Argon: Fluorescence Spectrum.—M. Berthelot.—(See p. 212).

Minimum Temperature Registered this Winter at the Summit of Mont Blanc.—J. Janssen.—The minimum temperature observed has been −43°.

Researches on Assimilable Nitrogen and on its Transformations in Arable Soil.—M. Pagnoul.—The experiments of last year lead to the following conclusions:—1. The rains, if abundant, may cause, on rich soils, a considerable loss of nitric nitrogen. 2. Vegetation covering the soil may hinder this loss, as has been already established by M. Dehérain. 3. Carbon disulphide, without killing the nitric ferment, arrests its action for the moment. 4. The ammoniacal forms seem to be a transitory state which organic nitrogen assumes when passing to the nitric state, and the carbon disulphide merely arrests it momentarily in this stage of its transformation. 5. The nitrous form may also be a transitory unstable state of the nitrogen passing from the organic to the nitric stage.

Presence of Helium in Clèveite.—P. T. Clève.—(See p. 212).

Definite Combinations of Metallic Alloys.—H. Le Chatelier.—The author has obtained and examined the tin-copper alloy, $SnCu_3$; the zinc-copper alloy, Zn_2Cu; the aluminium-copper, AlCu; and the chrome-zinc.

Aliphatic Aldehyds.—Louis Henry.—The intensity of the aldehydic character in the series examined by the author increases with the rise of the molecular weight.

Action of the Halogens upon Pyrocatechine.—H. Cousin.—The author has prepared and examined a trichlorocatechine, $C_6H_3Cl_3O_2$, and a bibromocatechine, $C_6H_4Br_2O_2$.

Siccative Properties of Fatty Matters in General, and their Transformation into Elastic Products Analogous to Lincxine.—If the distinction of the vegetable oils into driers and non-driers is exact, it is with the reservation that the oxidation of these oils is effected only at the ordinary temperature. The transformation into an elastic product analogous to that afforded by the drying oils can be effected in a general manner for all oils, vegetable or animal, if they are submitted to a suitable temperature.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 2, 1895.

Safety Valve for a Water Air-pump.—M. Berlemont.—This paper requires the accompanying figure.

Determination of the Molecular Weights of Liquids: Application to the Carbides.—Ph. A. Guye.—The author seeks to demonstrate that the determination of the molecular weight of a liquid may be referred to the knowledge of four constants, *i.e.*, the critical temperature, the critical pressure, and the temperature of ebullition at any given pressure. If this last temperature is referred to the atmospheric pressure, we have only to determine three constants. In certain cases it may be advantageous to determine also the molecular refraction. The author's results are given in the form of three tables.

Researches on the Dissociation of Mercuric Sulphate and Nitrate by Water.—Raoul Varet.—In the action of water upon mercuric sulphate, the reaction produced is that which evolves the greatest quantity of heat. This explains why this salt is decomposed by water into free acid and a basic salt, exothermic reactions; whilst it would be endothermic with alkaline or metallic salts which water does not decompose. In the dissociation of neutral mercuric nitrate by water the reaction ensues which is the least endothermic.

Certain Aluminium Compounds.—E. Schlumberger.—In this lengthy memoir we can merely notice the reactions with textiles and colouring matters. The various colloidal hydrates obtained do not seem able to play the part of mordants. A swatch of calico saturated with aluminium triacetate, and afterwards treated according to the methods used for fixing mordants of alumina, appears to fix the alumina only in a very imperfect manner. If dyed up in alizarin it takes a pale dull rose, not at all like a logwood red. If dyed in logwood it takes merely a dirty violet-grey. If we wish to obtain the reactions of the aluminous solutions with decoction of logwood, care must be taken to compare solutions which do not contain an excess of acid. We then have the following reactions:—*Normal aluminium acetate*, a red violet colour, warm and bright, the liquid remaining clear. *Trialuminium acetate*, dirty reddish grey colour; liquid turbid. Acetate obtained by heating the normal acetate to 150°, freed from excess of acetic acid by prolonged ebullition, remained coloured like onion skin. It has long been known what a pernicious action is exerted upon aluminous mordants, fixed but not yet dyed, by alkaline baths, even if incapable of dissolving alumina, such, *e.g.*, as milk of lime, and the equally degrading action of steam at 100° if prolonged. On reference to the foregoing, we shall find that the conditions destructive to the aluminous mordants are precisely those which favour the formation of trialuminium hydrate and of the more condensed hydrates. It appears, hence, probable that the degradation of the mordant observed in the cases mentioned is due to the formation of hydrates which are incapable of acting as mordants.

Researches on Mercury Nitrates.—Raoul Varet.—Nitric acid, like the sulphuric, picric, acetic, and oxalic acids, but unlike the hydrochloric and hydrocyanic acids, along with mercury oxide is displaced by the latter acids completely or appreciably.

Ethyle 3-Aminoanticrotonate and its Homologues.—R. Thomas-Mamert.—The author expounds the formation of the aminic derivative of acetylacetic ether. He shows that the stereoisomerism of the crotonic and isocrotonic acids must be necessarily and definitely admitted.

Combination of Hexamethyleneamine with Silver Nitrate, Chloride, and Carbonate.—M. Delepine.—It is remarkable to observe the combinations of a base with silver chloride and carbonate.

Researches on Pectase and Pectic Fermentation.—G. Bertrand and A. Mallèvre.—The ferment does not alone coagulate pectine. It effects this transformation only in presence of a soluble salt of calcium, barium, or strontium. The coagulum formed is not, as formerly supposed, pectic acid, but an alkaline-earthy pectate.

Volumetric Determination of the Mineral Salts of Zinc.—L. Barthe.—This paper will be inserted at some length.

MISCELLANEOUS.

Common Salt as a Fungicide. — According to the *Cape Agricultural Journal*, crops of wheat grown on soils containing 700 lbs. of chlorine in the soil, down to the depth of 6 inches, have been found free from rust.

The Cremometer. — MM. P. Cazeneuve and E. Haddon find, from a series of careful experiments, that the indications of the cremometer are not trustworthy for samples of milk which have been Pasteurised at 98° to 100°, with exclusion of air.—*Journal de Pharmacie et de Chimie.*

Royal Institution. — The Annual Meeting of the Members of the Royal Institution of Great Britain was held on May 1st, at the house of the Institution in Albemarle Street, Sir James Crichton-Browne presiding. The Annual Report of the Committee of Visitors for the year 1894, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Real and Funded Property now amounts to above £102,000, entirely derived from the Contributions and Donations of the Members, and of others appreciating the value of the work of the Institution. 62 new Members were elected in 1894, and 63 Lectures and 19 Evening Discourses were delivered in 1894. The Books and Pamphlets presented in 1894 amounted to about 242 volumes, making, with 578 volumes purchased by the Managers, a total of 820 volumes added to the Library during 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. Treasurer—Sir James Crichton-Browne. Secretary—Sir Frederick Bramwell, Bart. Managers—Sir Frederick Abel, Bart., K.C.B.; Captain W. de W. Abney, C.B. ; the Right Hon. Lord Amherst; Mr. William Anderson ; Sir Benjamin Baker, K.C.M.G. ; Messrs. John Birkett, William Crookes, Edward Frankland, Charles Hawksley, John Hopkinson, Alfred Bray Kempe, George Matthey; the Right Hon. the Marquis of Salisbury, K.G. ; Messrs. Joseph William Swan, Basil Woodd Smith. Visitors — Messrs. John Wolfe Barry, C.B., Charles Edward Beevor, M.D., Arthur Carpmael, Carl Haag, Victor Horsley, Hugh Leonard ; Sir Joseph Lister, Bart., M.D. ; Messrs. Lachlan Mackintosh Rate, Alfred Gordon Salamon, Felix Semon, M.D., Henry Virtue Tebbs, Silvanus P. Thompson, John Westlake, Q.C.; His Honour Judge Frederick Meadows White, Q.C. ; and Sir William H. White, K.C.B.

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.

Action of Hydrogen Peroxide on Ammonium Sulphide.—On the 23rd of February last, while removing the contents of his laboratory in Massachusetts, U.S., prior to returning to England, the writer noted two solutions oddly mixed in with apparatus and reagents. They were ammonium sulphide and hydrogen peroxide, the latter being a sample from the Oakland Chemical Co., of New York City. Hence it occurred to him to note their effect, if any, when brought together. The sulphide almost at once turned to an opaque yellow, due possibly to liberated sulphur. There was also a sensible rise of temperature, but the amount was not taken. In about 10 or 15 mins. the liquid got clear again and looked very like unaltered NH_4HS. Probably varying amounts of H_2O_2 would lead to varying results. As the writer has not, at present, the means of continuing his inquiries practically, he would be glad to receive information as to the nature of these changes, if they have already been investigated.—E. Rattenbury Hodges, Upper Holloway, N., April 24, 1895.

MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Arts, 8. (Cantor Lectures). "Recent American Methods and Appliances employed in the Metallurgy of Copper, Lead, Gold, and Silver," by James Douglas.
— Society of Chemical Industry, 8. "The Use of Hot Air in Drying," by C. C. Hutchinson. "The Estimation of Alkaline Salts in Fire Clays, Manures, &c.," by A. Cameron.
Tuesday, 7th.—Royal Institution, 3. "Alternating and Interrupted Electric Currents," by Professor George Forbes, F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8 30.
— Society of Arts, 4. "Recent Improvements in Designing, Colouring, and the Manufacture of British Silks," by Thomas Wardle.
Wednesday, 8th.—Society of Arts, 8. "The Extraction of the Rarer Metals from their Oxides," by Prof. W. C. Roberts-Austen, F.R.S.
— Geological, 8.
Thursday, 9th.—Royal, 4 30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Liquefaction of Gases," by Prof. Dewar, F.R.S.
— Institute of Electrical Engineers, 8.
Friday, 10th.—Royal Institution, 9. "A Recent Journey in Afghanistan," by the Hon. G. N. Curzon, M.P.
— Physical, 5. "On the Iodine Voltameter," by E. F. Herroun. "A New Method in Harmonic Analysis," by A. Sharp.
— Astronomical, 8.
Saturday, 11th.—Royal Institution, 3. "Music and Musical Instruments of the 16th, 17th, and 18th Centuries," by Arnold Dolmetsch.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1850.

IMMUNITY OF SOME LOW FORMS OF LIFE FROM LEAD POISONING.

By T. W. HOGG.

The earthworms which form the subject of this paper were obtained from the waste bark heap of the Elswick Lead Works. This heap consists principally of the old bark taken from the white-lead stacks, with a small proportion of sweepings from the yards; it now amounts to over 20,000 tons, and is the accumulation of over fifty years.

From the nature of the origin of this heap it is evident that, owing to the continual breaking off of small particles and powder from the brittle corroded sheets the bark will at length become impregnated with a considerable quantity of white-lead; this quantity varies to a small extent in different parts of the heap, but, generally speaking, the bark dried at 100° C. contains from 1·5 to 2·5 per cent of lead calculated as protoxide. Occasionally, however, somewhat larger proportions are met with, owing most likely to the fact that parts of the heap have been burnt, and the loss of the organic constituents of the bark sensibly increases the proportion of lead at those parts.

Away from the surface the bark is in a damp pulpy condition, and has to a great extent been converted into a kind of vegetable mould.

The composition of a good average sample is:—In original state, water = 50·20 per cent; dried at 100° C.:—

Carbon	45·60
Hydrogen	4·40
Oxygen with a small proportion of nitrogen, by diff.	29·50
Mineral matters other than lead ..	18·02
Protoxide of lead	2·48
	100·00

Notwithstanding that this partially decomposed bark heap would seem to offer an abundance of food for many organisms, the presence of so much lead would certainly lead one to suspect that it would not be a desirable residence for any of them.

It has therefore often been a matter of surprise to me to find that, especially in the summer time, this bark heap is a perfect hot-bed of life; it contains quite a considerable variety of organisms, the largest of which is the common earthworm.

I have examined these worms at different times, and have always found large quantities of lead in them. This would naturally follow from the fact that, although they will eat almost anything, even their own kind, they prefer food of a purely vegetable nature; this bark, therefore, undoubtedly supplies them with nutrition, and has, in consequence, ultimately been converted into its present disintegrated condition.

The intestines of the worms are always filled with finely-divided bark, and, if the whole organism is desiccated and dried at 100° C., the quantity of lead found corresponds very closely with that present in the bark itself.

The following are some of the determinations I have made in this way, the lead being stated as protoxide:—

A (1884)	.. ..	1·85 per cent PbO.
B ,,	.. ..	1·75 ,,
C ,,	.. ..	2·20 ,,
D (1891)	.. ..	2·45 ,,
E ,,	.. ..	2·48 ,,
F (1895)	.. ..	2·60 ,,

The earthworms themselves consist of approximately 80 per cent of water and 20 per cent of organic and mineral constituents. From these figures the percentage of lead in the living organism may be obtained as follows:—

A	0·37 per cent PbO.
B	0·35 ,,
C	0·44 ,,
D	0·49 ,,
E	0·496 ,,
F	0·52 ,,

Although this relatively large proportion of lead is present in each worm, the following experiments show that very little of it is retained or absorbed in its organs. Upon three separate occasions several worms had their intestines opened and thoroughly washed out; the quantity of lead was then ascertained in the worm freed from its intestinal matter, each determination being made upon 8 to 10 grms. The results now obtained were 0·009 per cent, 0·018 per cent, and 0·015 per cent respectively. Although this proportion does not appear to be very large, it is enormously greater than that found in any of the organs of the human adult who has died of lead poisoning. It is known that lead is chiefly absorbed by certain muscles and nerves, but for what reason no one has yet determined (Percy, "Met. Lead," p. 526). The most thorough investigation as to the quantity of lead present in the different organs has been conducted by Prof. Bedson ("Thorpe's Dictionary of Applied Chemistry," vol. ii., p. 445). Seventeen different organs were examined, and, although the largest quantity of lead was found in the liver, the largest proportion was present in the grey matter of the basal ganglion, this proportion being only 0·00053 per cent, and only about 1-25th of this proportion was found in the heart.

On account of the small weight of the organs of the earthworm, it would require an enormous number to be dissected in order to determine the relative proportion of lead absorbed by them. I have not made any attempt to do this. I have, however, dissected several, and treated them with a solution of ammonium sulphide to find if any part was specially darkened, and only in the case of the intestinal walls does this appear to take place.

Particular interest is attached to the calciferous glands. Darwin considers that the special function of these glands is to excrete lime. It occurred to me, therefore, to closely examine them, as they might also have something to do with enabling the worm to get rid of the large quantity of lead continually passing through it. Of course the glands are so minute that it would be impossible to determine the lead, if any, in them. On squeezing out the white pulpy matter upon a glass slide, and examining it under the microscope, treatment with ammonium sulphide failed to reveal the slightest evidence of their containing lead in any form. It is evident, therefore, that these worms are able to allow large quantities of lead to be continually passing through them. But it is not impossible that, during the somewhat long period the heap has been in existence, the worms have by successive generations evolved a special type, capable of withstanding the noxious effects of the lead. I should perhaps mention here that large worms are not often met with; they are generally of a very small kind (probably *Lumbricus minor*).

I have tried one preliminary experiment to ascertain the effect of white-lead upon fresh healthy earthworms, and placed several of them in large trays with good soil mixed with 1, 3, 4, and 5 per cent of white-lead; the soil was kept damp by daily adding a little water. These worms all lived for about two months; near the end of

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* A Paper read before the Society of Chemical Industry, Newcastle Section, February 28th, 1895.

this time several of them disappeared and the remainder became very inactive, but I think they lost their vigour more through want of food than through any deleterious effect the white-lead had upon then.

We have no means of judging how large a quantity of earth a single worm ejects during the year. Darwin roughly estimates this at 20 ozs. Taking this figure and the ordinary weight of a worm to be about 1½ grms., without any attempt at great accuracy, if a man possessed similar freedom from the noxious effects of white-lead, he would be able to swallow annually ten times his own weight of white-lead, and also to retain continually one pound of it.

In concluding this short paper, I have only intended to bring this subject forward in its present form as an additional instance of the immunity of certain organisms from the action of substances intensely poisonous to others. In connection with this highly interesting subject of immunity, perhaps it may not be out of place to briefly mention that we are now acquainted with organisms that continue to live in that most powerful destroyer of dead organic matter, potassium permanganate; with Algæ that live and are reproduced in arsenical solutions, and also assimilate arsenic from its solutions. There is a bird (*Buceros Rhinoceros*) that is reputed to eat nux vomica with impunity. Certain organisms are not affected much, if at all, by dilute solutions of mercuric chloride; and other more familiar instances will no doubt occur to those interested in such matters.

In connection with this subject I may mention that, some time ago, whilst experimenting with Carey Lea's silver solutions, I observed that moulds and bacteria grow and are reproduced in them after the introduction of a suitable food, and in the presence of so much silver that were it combined to form a soluble salt such as the nitrate, it would be quite impossible for anything to live in it. This latter subject seems to give promise of interesting results, and I may bring it before the Society upon some future occasion.

A CHEAP FORM OF SELF-REGULATING GAS GENERATOR.*

By W. W. ANDREWS.

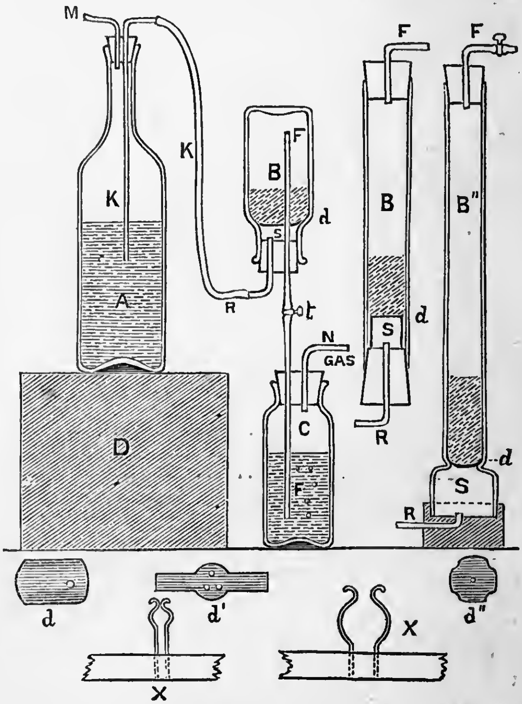
This form of generator is so cheap and easily set up that it makes it possible for every teacher and experimenter in chemistry to have, at practically no expense, a set of generators capable of yielding, whenever called upon, a supply of hydrogen, hydrogen sulphide, chlorine, carbon dioxide, sulphur dioxide, &c. It consists of an ordinary bottle, A, to serve as reservoir for the acid; a smaller bottle, B, which is the generator proper; and C, the familiar wash-hottle. A is closed by a cork holding two pieces of glass tubing; the one, M, just pierces the cork, and the other, K, reaches down a short distance below the surface of the acid and is connected by means of a rubber tube with R, thus forming a syphon leading from A to B, as shown in cut. The tube M is used to start the syphon K R by blowing into A while the stopcock, *t*, is open. F is the exit tube for the gas. The charge of solid in B rests on a shelf of sheet lead, *d*, the width of which equals the diameter of the neck of the bottle, and its length the internal diameter of the bottle. It serves the purpose of securing a space, S, which prevents the extra gas generated, when *t* is closed, from pressing the acid out of the syphon. Instead of a bottle for holding the charge a calcium chloride tube, or an Argand lamp chimney, with its larger end closed with a cork or sunk into a wooden block and cemented with paraffin wax, or even a piece of large-sized tubing may be used. If the last be used the space S is secured by cutting the lead in the shape *d'* and bending it to form a bench to support the solid charge, as shown. *d''* is the shape of the lead support to be used in the calcium chloride tube or Argand chimney. X and X' are the wire springs for holding B to its support, from which it may be lifted or replaced instantly. One is to enclasp the body, and the other the neck of the bottle or one of the glass tubes below the cork.

The advantages of this form of generator are:—

1. Its cheapness. An ordinary fruit-juice bottle and two wide-mouthed eight-ounce bottles will, with the necessary tubing, make one of good capacity.

2. Its convenience and safety. It is strictly self-regulating. If a rubber tube fitted with a glass plug ½ inch long, instead of a stopcock, be used, the gas flows only when the fingers pinch up the rubber along one side of the plug and ceases the moment they are lifted. The apparatus, therefore, is self-closing. It is very easy to re charge either with acid or solid.

3. It ensures a more even quality of gas than the well-known Kipp, and as complete utilisation of the acid as the Koninck generator. When the gas presses the acid back from B, it enters A laden with dissolved solid, and, on account of its greater specific gravity, it falls in a straight line to the bottom, where it spreads out in a dense layer. When the apparatus is again set working the purest acid is drawn from the upper layers. There is, consequently, some advantage in using a tall bottle for A.



4. It may be put together in a form which has all the advantages possessed by the Schanche generator (see *Journ. Amer. Chem. Soc.*, Dec., 1894), making the glass tube R long enough to reach to the top of B, and to curve a little downward, so that the acid may drop on the top of the solid charge and trickle through it. A drainage-tube with stopcock must be inserted into the cork to carry off the used-up acid from the space S. The inverted bottle for B possesses this advantage over the calcium chloride tube or chimney, viz., that owing to the position of the mouth of the gas exit tube, F, solid particles are not so likely to be shot into it when the acid is vigorously attacking the solid charge.

5. The pressure can be regulated at will by placing A at different heights, and this pressure may, at any moment, be reinforced by blowing into A, and the reinforcement held by closing M by means of a rubber tube and pinchcock.

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* *Journal of the American Chemical Society*, vol. xvii., No. 4, April, 1895.

VARIATION IN THE AMOUNT OF FREE AND ALBUMENOID AMMONIA IN WATERS, ON KEEPING.

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

In the course of an investigation into the quality of the Sydney Water Supply, 1875, I had noticed variations in the amounts of ammonia after keeping, and in order to obtain satisfactory and trustworthy data with respect to such changes, *i.e.*, as far as they were determinable by Mr. Wanklyn's process, samples of water were put up with the utmost care, and the amount of ammonia determined from time to time, a separate bottle being opened for each determination.

When waters were artificially made impure, the admixture was effected in a large glass pan, well stirred and otherwise mixed, and then transferred to clean clear quart bottles which were filled to the top and the excess squeezed out by the stopper.

The results, in the following Tables, show very clearly that, in some cases, the amounts of free and albumenoid ammonia increase and then decrease, and occasionally increase again; these changes are much more strikingly shown in the curves than in the tables; until decomposition and other natural changes have taken place, the potassium permanganate process fails to set free a large proportion of the albumenoid ammonia from the organic matter, so that a water might wrongly be declared pure if examined when freshly collected, or after lengthened keeping.

These following series of experiments were carried out as far back as 1876 with the aid of my then assistant, Mr. J. M. Muir, afterwards University Demonstrator.

I have hitherto refrained from publishing this investigation as I had hoped to extend the results in other directions, but as it may be some time before additional experiments can be undertaken, I present those already obtained. These, however, as far as they go, show how very important it is that the reports on the analysis of water should state how many days, weeks, or months have elapsed since the samples were collected.

The temperatures given in the table were taken at 9 to

TABLE I.

Nine Bottles each of Garden Tank, Laboratory Tank, and Distilled Water.

(Put up on October 9th, 1876).

Tempera ure F.				Garden Tank.		Laboratory Tank.		Ordinary Distilled Wa'er.	
				Parts per 1,000,000		Parts per 1,000,000		Parts per 1,000,000	
Morning. °	Evening. °	Nos.	Date. Oct.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.
68	70	1	11	0·01	0·09	0·35	0·184	0·07	0·04
68	70	2	12	0·005	0·042	0·25	0·08	0·09	0·036
68	69	3	13	0·01	0·04	0·24	0·094	0·05	0·03
65	66	4	14	0·01	0·04	0·22	0·11	0·07	0·03
67	67	5	16	0·01	0·054	0·23	0·096	0·04	0·01
71	71	6	17	0·01	0·04	0·23	0·08	0·04	0·005
70	68	7	19	0·005	0·03	0·22	0·06	0·04	0·005
70	70	8	20	0·005	0·02	0·22	0·084	0·03	0·005
71	70	9	21	0·005	0·02	0·21	0·07	0·005	0·005
								(Nov. 1).	(Nov. 1).

In all of these, with slight variations, there was a gradual improvement on keeping. The Laboratory tank at the time of these experiments was supplied with rain-water from the slate roof of the main building. The garden tank (underground) was also supplied from the same source. It is noticeable that there are considerable differences between the Laboratory tank and the underground garden tank waters although from the same roof.

TABLE II.

Five Bottles each of Garden Tank, Laboratory Tank, and Distilled Water.

(Put up on October 18th, 1876).

Temperature °F.				Garden Tank.		Laboratory Tank.		Ordinary Distilled Water.	
Morning.	Evening.	Nos.	Date.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.
67	65	1	Oct. 18	0·005	0·04	0·018	0·07	0·036	0·002
70	68	2	,, 19	0·005	0·03	0·13	0·06	0·03	0·005
72	70	3	Nov. 1	0·005	0·01	0·15	0·06	0·005	0·005
76	78	4	,, 16	0·005	0·01	0·15	0·06	0·005	0·005
71	73	5	,, 20	0·005	0·005	0·14	0·06	0·000	0·005

NOTE.—Heavy rain fell for about two hours on the morning of the 18th, just before collecting these samples.

TABLE III.

Seven Bottles each, Garden Tank, Laboratory Tank, and Distilled Water.

(Put up on October 23rd, 1876).

Temperature °F.				Garden Tank.		Laboratory Tank.		Ordinary Distilled Water.	
Morning.	Evening.	Nos.	Date.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.
72	70	1	Nov. 1	0·005	0·01	0·06	0·04	0·005	0·005
72	75	2	,, 21	0·005	0·005	0·04	0·05	0·005	0·005
74	76	3	,, 22	0·005	0·005	0·04	0·04	0·01	0·005
75	76	4	,, 23	0·005	0·005	0·04	0·05	0·01	0·005
68	67	5	,, 25	0·005	0·005	0·06	0·05	0·005	0·005
68	69	6	,, 28	0·005	0·005	0·07	0·03	0·005	0·005
67	68	7	,, 30	0·005	0·005	0·06	0·03	0·005	0·005

NOTE.—No rain since October 18th.

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* Read before the Australasian Association for the Advancement of Science, Brisbane, January, 1895.

10 a.m. and 4 to 5 p.m.; they were recorded because more rapid changes might be expected in warm than in cold weather.

I may remark that the determinations were made as recommended by Mr. Wanklyn, and that the sodium carbonate used for the free ammonia and the potash and potassium permanganate used for the albumenoid ammonia were boiled until they yielded distillates free from ammonia, and the distilled water used was also distilled from potash and potassium permanganate until free from ammonia.

(To be continued).

ACTION OF NITRIC ACID ON THE LIGNO-CELLULOSES.

By E. C. C. BALY and J. C. CHORLEY.

From the researches of Cross and Bevan, the results of which are summarised in a recent monograph ("Cellulose," Longmans, London, 1895), it is evident that the ligno-celluloses are not *mixtures* of cellulose and "incrusting substances," but ethereal compounds of cellulose with the complex of groups which may be conveniently included in the term "non-cellulose."

The interaction of the ligno-celluloses and dilute nitric acid which has been investigated by these chemists (*Berl. Ber.*, 1891, 1772; *Proc. Chem. Soc.*, xcvi., 61) has been shown to occur in the main between the acid and the latter complex, the cellulose being merely separated as an unaltered residue. The most prominent feature of the reaction is this sharp separation of the two groups of constituents; but the greater interest attaches to the elucidation of the complicated reactions by which the non-cellulose groups are entirely hydrolysed to soluble derivatives. This task we have undertaken: our investigations being devoted, in the main, to a quantitative account of the gaseous product. It had been previously established (*loc. cit.*):—1. That the most characteristic of their products are nitrous oxide and hydrocyanic acid, indicating as they do the direct union of nitrogen to carbon. 2. That the specific decomposition depends upon the presence of nitrous acid and is entirely arrested by the addition of urea. 3. That the destructive oxidation of the non-cellulose is limited to a very small proportion of its constituent groups, the reaction being completed with relatively small proportions of the acid at considerable dilutions (3 to 5 per cent HNO_3), and at low temperatures; further, the proportion of gaseous carbon compounds formed in the reaction is relatively small. 4. Lastly, that the proportion of N in combination with the non-cellulose groups, at any period of the decomposition is relatively small.

In our experiments we have taken beech wood as representing the class of fully lignified fibres; the proportion of nitric acid usually 33 per cent (HNO_3) of the weight of the wood in 10 per cent aqueous solution, and the conditions four to five hours heating in the water-bath, which takes the decomposition to the extreme limit, *i.e.*, with almost complete elimination of the N in the form of gaseous products.

The gaseous products of the decomposition being CO, CO_2, N_2O_4, N_2O, N_2, HCN, this separate estimation involved no small analytical difficulties.

The following are the actual details of the experiments:—

10 grms. of wood were placed in a flask together with 35 c.c. of 9·64 per cent HNO_3, immersed in a water-bath, and the products led through absorption vessels as follows:—

(*a*) Dilute sulphuric acid to which a standardised solution of potassium permanganate was added continuously in slight excess (estimation of N_2O_4+HCN jointly).* (*b*) The gas was then dried over calcium chloride, and passed through (*c*) weighed tubes containing soda-lime (estimation CO_2). (*d*) The remaining gases were collected over mercury and analysed by the following methods:—

1. N_2O_2, after adding O and absorption of N_2O_4.
2. CO. A known volume of H was added, and after explosion and absorption by KOH the CO was calculated from the total contraction. It was assumed that H and O combine by preference to the exclusion of the N_2O.
3. N_2O. A second explosion gave the data for calculating the proportion of this gas.
4. N_2 was calculated from the original gas.

Before commencing the whole of the apparatus was, as far as possible, exhausted of air.

In (*a*) the strength of the potassium permanganate solution was such that 1 c.c. was equivalent to 0·05 grm. NO_2. 25 c.c. of this were used, and the excess titrated with iron solution; this excess was 1·93 c.c., so that the solution used was 23·07 c.c., equivalent to 1·153 grms. NO_2, but which represents both the HCN and NO_2. In a collateral experiment the total HCN was estimated as AgCN and found to be 0·116 grm., which is equivalent to 0·395 grm. of NO_2, leaving 0·758 grm. NO_2 actually evolved (subject to a further correction which follows later). The CO_2 estimated by the increase of weight in the soda-lime tube (*c*) was 0·268 grm.

The gas in the gas-holder was 350 c.c. at 16° and 757 m.m., which was analysed as below.

The N_2O_2 was estimated by the contraction in volume resulting from the absorption of N_2O_4 formed on the addition of a known volume of O.

A known volume of H was then added and the gas mixture exploded. From the contraction in volume and absorption by KOH the CO was estimated; it was assumed that the H and O combined in preference to the H and N_2O. After further addition of H, the mixture was again exploded and the N_2O calculated.

From the volume of the residual gas the N could be calculated. In an actual experiment the following were the numbers obtained:—

	C.c.
Original volume of gas	5·67
Oxygen added	2·95
Volume after absorption by KOH	6·77
Hydrogen added..	0·95
Volume after explosion and KOH	5·45
Hydrogen added..	10·48
Volume after explosion	9·95

Calculation.—Contraction due to the absorption of NO_2=1·85 c.c.; this=1·23 c.c. of NO and 0·62 c.c. of O used (*a*). The contraction after the first explosion=2·27 c.c.; of this, 0·95+3÷2=1·42 is due to the H_2O; therefore contraction due to the CO_2=0·85 c.c.; this gives 0·56 c.c. of CO and 0·28 of O used (*b*). The O combining with the H being 0·47 c.c. The total O used is, therefore, 0·28+0·47+0·62=1·37 c.c. The O left is therefore 2·95 − 1·37 = 1·58 c.c. After the second explosion the total contraction was 5·98 c.c.; of this, 4·74 is due to the 1·58 c.c. of O left; therefore the contraction due to the N_2O=1·24 c.c. Now, the H added was 10·48 c.c.; of this, 3·16 c.c. was used by the O, and 1·24 c.c. by the N_2O. The total H used=1·24+3·16=4·40 c.c.; the H left was, therefore, 10·48−4·40=6·08 c.c. The N formed by the decomposition of the N_2O=1·24 c.c.; therefore the N originally present in the gas was 9·95−6·08−1·24=2·63 c.c.

	C.c.	Per cent.
N	2·63	46·36
N_2O	1·24	21·87
NO	1·23	21·69
CO	0·56	9·87
	5·66	99·79

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* The HCN was separately estimated in independent experiments as AgCN (*infra*).

The N in this analysis is too high, owing to the presence of a small quantity of air originally present in the apparatus, in amount about 14 c.c., and, of course, being the first gas to enter the holder the numbers obtained must therefore be corrected as under.

	Per cent.
N .. .. —	=44·2
N_2O	=22·8
NO	=22·6
CO	=10·3
	99·9

In calculating the results to the original weight of interacting substances—wood and nitric acid—the gas remaining in the absorption vessels and flask had to be taken into account, and on the assumption of more or less uniform composition.

1. The volume of the soda-lime tubes (*c*) with connections .. .. = 30 c.c.
2. Between these and the surface of the $KMnO_4$ solution .. .. = 145 ,,
3. The volume of the flask less wood and acid .. .. = 400 ,,

The volume of the gases were measured at 16° and 767 m.m., except the gases in the reaction flask, which were at 95°. The gas having the composition of that analysed was 350+30 c.c. =380 c.c. from (1), and to this must be also added 144 c.c. CO_2, being that absorbed by the soda-lime. Between the soda-lime tube and the $KMnO_4$ solution there were 145 c.c. of gas (2) containing CO_2; this, by calculation, contains 40 c.c. CO_2, leaving 145 − 40 = 105 c.c. of analysed gas. The total CO_2 which passed the $KMnO_4$ = 144+40=184 c.c. So that a total of 669 (380+184+105) had passed through the $KMnO_4$. Now, 400 c.c. of gas was left in the flask at 160 m.m. and 95° =62 c.c. at 0° and 760 m.m. Between this 62 c.c. and the 669 c.c. the HCN must be proportionately divided, *i.e.*, 88 c.c. HCN have been absorbed by the $KMnO_4$ and 8 c.c. left in the flask; 88 c.c. HCN=0·364 grm. NO_2; therefore = 1·153−0·364=0·789 grm. is the true amount of NO_2 given off by the wood.

54 c.c. are left in the flask, which must contain 15 c.c. of CO_2, leaving 39 c.c. of gas as analysed.

Total analysed gas is, therefore, 380+105=485 c.c. at 16° and 757 m.m. + 39 c.c. at 0° and 760 m.m.=494 c.c. at 0° and 760 m.m., less 14 c.c. of N from air present =480 c.c. The total CO_2=184+15 c.c.=199 c.c. at 0° and 760 m.m.

	Results. C.c.	Per cent relation.	Weights. Grms.	Containing N. Grms.	Containing C.
N_2	212	18·3	0·266	0·266	
N_2O.. ..	109	9·4	0·215	0·137	
N_2O_2 ..	108	9·3	0·144	0·067	
N_2O_4 ..	383	33·2	0·789	0·240	
HCN ..	96	8·3	0·116	0·060	0·051
CO_2	199	17·2	0·393		0·107
CO	49	4·3	0·061		0·026
	1156	100·0	1·984	0·770	0·184

In regard to the accuracy of the results contained in the above Table: the CO_2, HCN, and N_2O_4, being estimated directly, the results may be taken as correct within the limits of the ordinary errors.

In calculating the remainder it was necessary, as stated, to make certain assumptions, to which larger errors attach. The degree of approximation may be estimated by taking the statistics of nitrogen: the N as HNO_3 taken was 0·750; the N calculated from the estimated volume of N and N compounds evolved is 0·770. Taking into account the unusual complications involved, and the purpose of this section of our observations, the results are sufficiently close to establish the main features of the decomposition.

First. The N_2O_4 and N_2O_2 representing 52·4 per cent of the N of the HNO_3 taken, it is evident that the proportion of nitric acid undergoing complete deoxidation is 20 per cent on the wood.

Second. The wood substance may be taken as containing approximately 50 per cent C. Of 4·5 grms. C., therefore, in 9 grms. wood, 0·133 is destructively oxidised to gaseous compounds—*i.e.*, only 2·95 per cent.

Before drawing final conclusions as to the mechanism of the reaction, we have to deal with the remaining products.

In the experiment described above the following were estimated:—

(*a*) *Fibrous Residue:* the ultimate fibres of the wood in the condition of approximately pure cellulose	48·00
(*b*) *Volatile Acid:* chiefly acetic, calculated as acetic	11·80
(*c*) *Oxalic Acid:* precipitated as Ca salt in acetic acid solution..	3·84
(*d*) *Soluble Derivatives of Non-cellulose:* ..	26·16
	89·80

(*a*). Of this "cellulose" residue little need be said. It contains oxycellulose groups, giving, on distillation with hydrochloric acid (1·06 sp. gr.), 4·5 per cent furfural. On treatment with nitrating acid a highly nitrated product was obtained. The following experiment, carried out comparatively with cotton, may be cited:—

	Yield p. c. in cellulose.	P. c. N in product.
Beech cellulose	170·4	12·91
Cotton	174·0	12·96

On treatment with HNO_3, of 45 sp. gr. alone—immersion for three minutes, followed by cold water:—

Yield of nitrate, 140·3 p.c. N p.c. in nitrate, 11·0.

(*b*). The *Volatile Acid.*—A large number of determinations of these products were made, the proportion of acid to wood being varied, and also the duration of the digestion. In cases where the soluble products contained NO residue, the solutions were treated with iron (wire) in presence of sulphuric acid, and distilled. The distillates, free from N acids, were titrated with normal soda solutions. The yields varied from 8 to 12 per cent, calculated as acetic acid. In some cases the solutions were oxidised with permanganate before distillation: the yields of volatile acid were, however, not increased.

Comparative experiments were also made with other typical ligno-celluloses. Jute, which has the same general features as beech-wood, gave similarly higher yields (12 per cent). Pine wood, on the other hand, representing a totally different type of lignification, gave low yields (3 to 4 per cent). These results agree with those obtained in destructive distillation.

(*c*). The *Oxalic Acid* is present in small proportion (3 to 4 per cent of the wood). Taken together with the CO_2 and CO, as representing jointly the products of destructive oxidation, the proportion of the ligno-cellulose undergoing this complete resolution may be taken at about 10 per cent.

(*d*). On evaporating the solution of the soluble by-products of the reaction, a yellow gummy residue is obtained—a mixture of ill-defined bodies of pronounced acid characteristics. All attempts to convert this complex into the well-defined dibasic acids—of the dimensions of C_6 or C_5—have failed. On further oxidation with nitric acid, under carefully regulated conditions, there is a considerable further formation of oxalic acid with volatile acids and oxides of carbon.

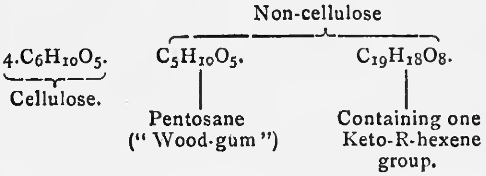
By fusion with the alkaline hydrates at 250°, the complex is resolved into carbonic, oxalic, and acetic acids. No aromatic products are formed.

As directly obtained in the original reaction, the products retain many of the essential characteristics of the non-cellulose constituents of the original wood—notably the property of condensation to furfural.

It appears, therefore, generally that in the original reaction the first groups to be attacked are the keto-R-hexene molecules of the ligno-cellulose: these ultimately undergo destructive oxidation. The more easily hydrolysable groups—*e.g.*, pentosans and β-celluloses—are next attacked, and are dissolved with more or less attendant oxidation, according to the duration of temperature of the reactions.

Without attempting an exact formulation of the reactions, the numerical relationships thus established may be summed up in approximate molecular ratios as follows:—

The ligno-cellulose may be regarded as—



$$\underbrace{4.C_6H_{10}O_5.}_{\text{Cellulose.}} \qquad \overbrace{C_5H_{10}O_5. \qquad C_{19}H_{18}O_8.}^{\text{Non-cellulose}}$$

Pentosane ("Wood-gum") — Containing one Keto-R-hexene group.

Taking into account only the HNO_3 deoxidised to N_2O+N_2, the molecular ratio is $6HNO_3$.

The reaction consists then, in the main, in the destructive oxidation of the one keto-hexene group of the non-cellulose complex; the acetic acid being formed partly from this group, with CH_3 residues obtained from groups in combination.

The nitric acid is broken down as below:—

$$12HNO_3 = 6H_2O + 4N_2 + 2N_2O + 14O_2.$$

Taking an approximate formula, $C_6H_6O_3$, for the hexene group, and allowing for the destructive oxidation of the C_6 nucleus, with the attendant union of COOH to CH_3, the molecular proportion of these characteristic products is—

$$2.C_2H_4O_2 : 4[CO_2,CO,C_2H_2O_4],$$

i.e., of the 6 carbons 2 are split off as acetic acid; the remainder are similarly oxidised, and after oxidation two are liberated in the simpler forms, and two remain in the residual solution.

The remaining groups of the complex ligno-cellulose formulated above are resolved as follows:—

The cellulose is separated insoluble in the approximate ratio* $4C_6H_{10}O_5$; the pentosan is dissolved, and the residues of the lignone complex also hydrolysed and dissolved.

Under the conditions of action described above the resolution is complete; the reaction may, on the other hand, be easily regulated to any desired limit, and the isolation of the cellulose completed by treatment with alkaline solutions.

The reactions, however, retain their specific characteristics through a wide range of variations of the conditions: in all cases it is the unsaturated groups, specially characteristic of the lignified celluloses, which are selectively and specifically attacked.

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London, W.C.

Laboratory Apparatus for Fractionated Distillations.—P. Monnet.—The apparatus cannot be described intelligibly without the accompanying full-page plate. The essential novelty is that the vapours are exposed to filings or fragments of metal. The author has used small shot (No. 6), though for very volatile liquids other sizes may be introduced, each kind separated from the others by means of copper gauze.—*Bull. de la Soc. Chim. de Paris*, xii.-xiv., No. 3.

ON THE

PHOTOGRAPHY OF THE HIGHEST RAYS OF THE SPECTRUM.*

By VICTOR SCHUMANN, Leipzic.

"April 28th, 1895.

"At the commencement of this month I have, for the first time, photographed the spectrum of air far beyond the wave-length 180·0 Angström's scale, and have found that air, notwithstanding its untransmissiveness for the shortest wave-lengths, develops an astonishing energy. For instance, one of these photographs of the air, in a length of 34 m.m., shows more than fifty bands, all shading off towards the red. I have resolved many of these bands into lines.

"My present photographs of the hydrogen spectrum have shown a greater wealth of lines than might have been expected from my former estimate (600 lines). I have resolved the district situate beyond w.-l. 180·0 Angström's scale into seven districts, each of 3 degrees in extent. The first three regions contain 750 lines; one of them, with a length of 13 m.m., 350 lines. At present I estimate the total number of the lines of this district at 1500 to 2000."

THE REDUCTION OF ALUMINA CONSIDERED FROM A THERMO-CHEMICAL STANDPOINT.†

By JOSEPH W. RICHARDS, A.C., Ph.D.

The writer is a firm believer in the usefulnes of thermochemical data as a guide in chemical experiment. However, the deductions drawn from these data are often incorrect, because all the conditions have not been taken into account. Berthelot has postulated the "law of maximum work," which affirms that every chemical reaction takes place with the maximum production of heat possible by the combination of the reacting substances. This law, however, is too limited; it leaves out of consideration altogether the disturbing effect of the relative masses of the substances, their physical condition, and the physical condition of the products. For instance, an excess of a reducing agent is often necessary to reduce an oxide, producing or causing to take place a highly endothermic reaction. Again, if one of the possible products of a reaction would be in such a physical condition as to be quickly and completely removed from the sphere of the reacting bodies, its formation will be greatly accelerated. If two solutions are mixed, and one of the possible products of their reaction is insoluble in the solution, this fact will determine the formation of that substance, even though the reaction is an endothermic one. The heat deficit will simply be made up by an abstraction of heat from the solution; it will be cooled. Similarly, if two solids or liquids, or a solid and a liquid, are brought into intimate contact, and the possible result of their reaction should be a gas, the reaction will tend to take place, even if endothermic, because the gas escapes from the field of reaction as soon as produced, and so the inverse reaction is prevented. In such a case, putting pressure on the substances would hinder the formation of gas and retard the reaction; removing the pressure would facilitate the reaction. It has been proved, experimentally, that mercuric oxide and carbon react at a lower temperature when warmed in a vacuum than when at ordinary pressure.

Another important point is, that there is, under a given pressure, a critical point of temperature at which reactions first take place, the explanation of which is that the

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* The cellulose differs, it may be again noted, from the typical cellulose of this formula, containing only 43·0 per cent C., and yielding 4 to 5 per cent furfural on boiling with hydrochloric acid.

* Extract from a letter to Mr. Crookes.

† Read before the Chemical Section of the Franklin Institute, February 19, 1895.

particles of the original substances are themselves bound together by chemical affinity, and that the molecular vibration corresponding to a certain temperature is necessary before the new affinities tending to produce the reaction can overcome the original affinities of the primary substances. At 555° C. the atoms of oxygen and hydrogen, in the molecules of their respective gases, are vibrating to such distances from their mutual centre of attraction, that the new affinity of the unlike atoms for each other is able to disrupt the original molecules, and combination occurs. Similarly, carbonic oxide can break up the oxygen molecule only at 655° C. These remarks apply to the free gases at ordinary pressure. Under other conditions, the oxidation can go on at different temperatures.

If the substances are brought to the critical temperature at which they react, and the reaction at that temperature is exothermic, then the exchange will take place and proceed of itself until complete. If the reaction is endothermic, the first reacting portions absorb heat from the rest and lower the temperature below the critical point, thus putting a stop to the reaction, the exchange starts again only when the temperature is kept up to the critical point by the liberal supply of heat from without. This is the *modus operandi* of the reduction of many strong oxides.

The heat of formation of a molecular weight of alumina (102 parts) was determined by Baille and Féry, by oxidising aluminium amalgam. The reaction is—

$$Al_2Hg_3+3O=Al_2O_3+3Hg=+392{,}600 \text{ calories.}$$

This is evidently the heat of oxidation of liquid aluminium to solid alumina, *minus* the heat of formation of Al_2Hg_3. This latter quantity is unknown, but is probably quite small. These investigators determined the heat of hydration of alumina; thus—

$$Al_2O_3+3H_2O=2Al(OH)_3+3000 \text{ calories.}$$

Berthelot, long previously had found the heat of formation of hydrated alumina to be 391,600 calories. This would give 388,600 for anhydrous alumina, but this figure is based on the oxidation of solid aluminium. To compare it with Baille and Féry's figures, we must *add* to it the latent heat of aluminium at 0° C., which is calculated as follows:—

		Calories.
Latent heat of 1 kilo. aluminium at the melting point		100·0
Heat given out by 1 kilo. of molten aluminium in falling from 625° to 0°=625 ×0·308 (sp. heat molten aluminium), determined by Pionchon	Cal. 192·5	
Heat given out by 1 kilo. of solid aluminium through the same range (writer's experiments)	158·3	
Decrease in the latent heat		34·2
Latent heat of 1 kilo. at 0° C.		65·8
The latent heat of 54 kilos. (Al_2) is, therefore ..		3550·0

Adding this to Berthelot's corrected value for anhydrous alumina from solid aluminium, the sum is 292,150 calories. This agrees so closely with Baille and Féry's figures that the latter are accepted as being very near the truth.

Concerning the reduction of this compound to metallic aluminium, two ways are possible—the direct and the indirect. By the first I mean the use of an agent which is powerful enough to reduce it to metal at a single step; by the indirect is meant, first, reducing alumina to a more tractable aluminium compound, and then reducing the latter. Leaving electricity entirely out of consideration, there are but very few reducing agents which can decompose alumina directly, and they only at very high temperatures. Sodium does not act on it at any temperature, since sodium oxide is a far weaker compound than alumina.

$$3Na_2+3O=3Na_2O+299{,}280 \text{ calories.}$$

If the alumina, however, is converted into an oxygen-free aluminium salt, its affinities are then much weaker, while the reducing-power of sodium is relatively much greater.

Chlorine and carbon together decompose alumina,—

$$Al_2O_3+C+6Cl=2AlCl_3+3CO.$$

Heat absorbed—		
Decomposing alumina		392,600
Heat liberated—		
Aluminium chloride	325,510	
Carbonic oxide	88,200	
		413,710
Excess of heat..		21,110

This reaction proceeds easily at a bright red heat; in fact, we not only have an exothermic reaction, but the products also are all gaseous, and as soon as the critical temperature at which the reaction begins is reached, the operation proceeds rapidly and completely.

The aluminium chloride is easily reduced by sodium, potassium, lithium, and magnesium, perhaps to a slight degree by manganese and zinc, which have about an equal affinity for chlorine. No other substances, organic or inorganic, besides these few rare alkaline and alkaline-earth metals, have a heat of combination with chlorine sufficient to decompose aluminium chloride.

Bromine and iodine vapours do not act like chlorine, and the reason is seen in casting up the thermal data. The difference between the heat of formation of alumina and 3 molecules of carbonic oxide is 392,600 − 88,200 = 304,400 calories. Against this, chlorine formed aluminium chloride and gave 325,510 calories, making the reaction exothermic by 21,110 calories. Bromine, however, in forming the bromide, gives only 243,550 calories, leaving a deficit of 60,850 calories, while iodine gives only 144,310, leaving a deficit of 160,190 calories. The only known way of making these compounds is directly from aluminium itself.

Sulphur, also, is unable, either alone or with the assistance of carbon, to split up alumina. The heat of formation of aluminium sulphide being 127,950 (from liquid aluminium), the enormous deficit of 304,400 − 127,950 = 176,450 calories, makes the reaction impracticable. However, when carbon bisulphide vapour is passed over white-hot alumina, aluminium sulphide is formed. It would appear at first sight as if the compound of carbon and sulphur would be less likely to produce the reaction than those elements uncombined; but the secret of this paradox is disclosed when we note that carbon bisulphide is one of the few endothermic compounds, absorbing 29,000 calories in its formation, and giving out just that amount in its decomposition. This helps to reduce the deficit by just so much. Further, carbonic oxide is not formed, but carbonyl sulphide, which has a heat of formation 4700 calories higher for each atom of oxygen taken up. Casting up the thermal data, we have—

$$Al_2O_3+3CS_2=Al_2S_3+3COS.$$

		Calories.
Heat absorbed—		
Decomposing alumina		392,600
Heat evolved—		
Formation of aluminium sulphide	127,950	
,, ,, carbonyl sulphide .	102,300	
Decomposition of carbon bisulphide	87,000	
		317,250
Heat deficit..		75,350

This is still a large deficiency, but the critical temperature for the reaction is a white heat, and, if the supply of carbon bisulphide is abundant, and the heating is kept up energetically, the reaction is practicable.

As for reducing this sulphide to metal, thermal data show us that only the alkaline and alkaline-earth metals can accomplish it easily, while manganese, zinc, tin, iron, and copper can do it to a small extent when used in large excess, making use of the influence of mass to bring about the endothermic reaction. This compound recommends itself more particularly for electrolytic decomposition. When mixed with an alkaline sulphide it forms an easily fusible double sulphide, which theoretically requires less than one volt to decompose it.

Alumina is easily converted into its fluoride, which, however, can only be decomposed chemically by the alkaline or alkaline-earth metals. Even fluorine alone acts energetically on it, raising it to incandescence.

The reaction—

$$Al_2O_3+6F=2AlF_3+3O$$

sets free $555{,}550-392{,}600=162{,}950$ calories, which accounts for the phenomena observed.

Even hydrofluoric acid gas can be used for the reaction, the splitting up of six molecules of gaseous hydrofluoric acid requiring, at 0° C., 222,600 calories, against which we have the formation of three molecules of water, 174,300 calories, leaving for the reaction a net excess of—

$$Al_2O_3+6HF=2AlF_3+3H_2O+114{,}650 \text{ calories.}$$

A reaction similar to this is impracticable with hydrochloric acid gas, and we find that it would be endothermic to the extent of about 30,000 calories.

Direct Reduction.

Minet has measured carefully the voltage required to decompose alumina dissolved in a fluoride bath, using a carbon anode, at which carbonic oxide is formed. As one volt represents a thermal value of 23,000 calories for each equivalent of oxygen liberated, it would represent $23{,}000\times6=138{,}000$ calories for each molecule of alumina split up. The number of calories represents, therefore, the thermal value of the following reaction:—

$$Al_2O_3+3C=Al_2+3CO$$

at the temperatures given. Minet's best experiments gave:—

Temperature.	Voltage.	Calorific equivalent (3O).
900°	2·40	331,000
1100°	2·17	299,460

If we can add to these numbers the heat evolved by the reaction $3C+3O=3CO$, at these temperatures, we shall obtain the value of the reaction Al_2+O_3, or the heat of oxidation of liquid aluminium to liquid alumina. This calculation is made as follows:—

$$C+O=CO+29{,}400 \text{ calories at } 0^\circ \text{ (Berthelot).}$$

Specific heat of carbon ($t>900^\circ$) $0{\cdot}53\times\frac{134{\cdot}6}{t}$ (a)

(Pionchon).

Specific heat of oxygen .. $0{\cdot}2114+0{\cdot}00001875\,t$ (b)

(Le Chatelier and Mallard).

Specific heat of carbonic oxide .. .. $0{\cdot}245+0{\cdot}0006\,t$ (c)

(Regnault).

Therefore,—

$$C+O\left(\begin{matrix}\text{at } t^\circ\\ t>900^\circ\end{matrix}\right)=29{,}400+(12a+16b-28c)\,t.$$
$$=27{,}785+2{\cdot}8824\,t-0{\cdot}0003\,t^2.$$

Substituting, we have—

At 900°, $C+O=30{,}136$ $3(C+O)=99{,}408$
At 1100°, $C+O=30{,}592$ $3(C+O)=91{,}776$

Adding these to the values of the reaction given by Minet's experiments, we have—

At 900°, $Al_2+O_3=331{,}000+90{,}408=421{,}408$ cal.
At 1100°, $Al_2+O_3=299{,}460+91{,}776=391{,}236$ cal.

Now, we know that at 0°, $Al_2+O_3=391{,}600$ calories, the only difference between this and the figures just derived being that the latter is calculated for *solid* alumina. For liquid alumina, we should have to subtract from it the latent heat of fusion of alumina. This is not known, but if we estimate it at 43 calories per kilo. (from analogy with other oxides), we may subtract $43\times102=4400$ calories. We then have the heat of formation of liquid alumina from liquid aluminium, as follows:—

	Calories.
0°	387,200
900°	421,408
1100°	391,236

It will be noticed that the value has reached a maximum between 0° and 900°, and is rapidly decreasing; in other words, above 1000° alumina rapidly becomes easier to decompose. A curve passing through the above values would be of the following form:—

$$Q=387{,}200+192{\cdot}6\,t-0{\cdot}1716\,t^2.$$

The question now is—At what temperature would the heat of oxidation of our reducing agents equal the heat of formation of alumina? We may fairly assume that if that point is above the critical point for the reaction, reduction will there begin.

Carbon.—The formula for the heat of oxidation of carbon to carbonic oxide has already been deduced. We therefore have—

$$Al_2+O_3=387{,}200+192{\cdot}6\,t-0{\cdot}1716\,t^2$$
$$3(C+O)=83{,}355+8{\cdot}6472\,t-0{\cdot}0009\,t^2$$

When these two expressions become equal to each other,

$$t=1980^\circ.$$

If liquid carbon is the reducing agent, its efficacy is about 21,000 calories greater than solid carbon, and—

$$t=1940^\circ.$$

As verifying these calculations, I may refer to the fact that liquid alumina is, beyond a doubt, reduced by carbon in electric furnaces, because the output of aluminium is greater than the number of ampères passing through the furnace could theoretically produce, and, also, because decomposition can be produced by a rapidly-alternating current, where electrolysis is out of question. The temperature in such furnaces is probably about 3000°. Again, in a Pennsylvania iron blast-furnace, in which the temperature is almost certainly not over 2000°, as much as 1 per cent of aluminium has been reduced into the iron. The liquid carbon in the iron in the crucible is here the reducing agent, reducing aluminium from a slag carrying as high as 25 per cent of alumina.

It thus appears that both calculation and practice unite in showing that carbon begins to reduce alumina in the neighbourhood of 2000° C.

Hydrogen.—

$H_2+O=69{,}000$ calories (to liquid H_2O at 0°)
$=58{,}100$,, (to vapour of water at 0°)
Specific heat of hydrogen $=3{\cdot}3820+0{\cdot}0003\,t$ (a)
,, ,, oxygen $=0{\cdot}2114+0{\cdot}00001875\,t$ (b)
,, ,, water vapour $=0{\cdot}4208+0{\cdot}000182\,t$ (c)

$$H_2+O\,(\text{at } t^\circ)=58{,}100+(2a+16b-18c)t$$
$$=58{,}100+2{\cdot}572\,t-0{\cdot}0024\,t^2.$$

We therefore have:—

$$Al_2+O_3=387{,}200+192{\cdot}6\,t-0{\cdot}1716\,t^2$$
$$3(H_2+O)=174{,}300+7{\cdot}716\,t-0{\cdot}0072\,t^2$$

When these two expressions become equal to each other,

$$t=1790^\circ.$$

This is just about the melting-point of platinum, and may appear lower than can possibly be the fact; nevertheless, Mr. H. Warren, in England, has recently succeeded in reducing alumina to aluminium in a current of hydrogen gas, the alumina being inside a lime tube heated on the outside by the oxy-hydrogen flame. It is hardly possible that the temperature inside the tube could have exceeded 2000°, yet complete reduction to metallic globules was obtained.

This second confirmation of the calculations by experiment induces me to add, in conclusion, the following observations:—

Acetylene gas, C_2H_2, has a negative heat of formation of 51,500 calories. It is, therefore, just by that much a more powerful reducing agent than C_2 and H_2 alone. The equation is—

$$Al_2O_3 + C_2H_2 = Al_2 + 2CO + H_2O.$$

The thermal equations are—

$$\begin{array}{lcll} Al_2 + O_3 & = & 387{,}200 + 196{\cdot}2\,t - 0{\cdot}1716\,t^2 & (a) \\ \hline 2(C + O) & = & 55{,}570 + 5{\cdot}7648\,t - 0{\cdot}0005\,t^2 & (b) \\ H_2 + O & = & 58{,}100 + 2{\cdot}572\,t - 0{\cdot}0024\,t^2 & (c) \\ C_2 - H_2 & = & 51{,}500 & (d) \end{array}$$

making $b+c+d=a$.

$$t = 1870°.$$

I am inclined to think that this highly endothermic compound would reduce alumina at an even lower temperature than this, because we have not only the benefit of its great heat of decomposition, but we also have, at the moment when it decomposes, the carbon and hydrogen atoms *in statu nascendi*, and we thus have all the advantages of a *nascent* reducing agent. I need not, to an audience of chemists, expatiate on the greater chemical activity of a nascent reducing agent.

The recent developments in the manufacture of calcium carbide and acetylene open up a possibility in the way of reducing alumina which may bear fruit. Allow me, at least, to claim for thermo-chemistry, rightly understood, that it is a most helpful guide to intelligent experiment.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

The Exhibition of Scientific Apparatus and Processes at the Conversazione of the Royal Society, on Wednesday, May 1st, included some objects of exceptional interest.

Prof. Roberts - Austen, C.B., F.R.S., exhibited an electrical furnace used for fusing chromium, titanium, and other refractory metals. It consists of a fire-clay case lined with magnesia, and containing a magnesia crucible. The carbon poles are horizontal, and the arc is bent down upon the object to be heated by means of a magnet. For purposes of exhibition, an image of the molten contents of the crucible is projected upon a screen by means of a mirror and lens. The current is about 60 to 70 ampères at 100 volts.

The world-famed metallurgists, Messrs. Johnson, Matthey, and Co., exhibit a nugget of platinum, 158 ozs.; an ingot of palladium, of 1000 ozs.; a rhodium ingot, of 72 ozs.; osmium, both molten and as a sponge; ruthenium, fused by the arc; and pure iridium, in a rolled sheet.

Prof. Ramsay exhibited the spectra of argon, and of helium mixed with argon. There were shown spectra of argon obtained from air, and those of a mixture of argon and helium as extracted from the mineral clèveite. The sodium flame was shown to demonstrate the non-identity of the D_3 line of helium with the D_1 and D_2 lines of sodium.

Sir B. W. Richardson exhibited an electrical cabinet for hospital service, thus proving that medical electricity is not the exclusive property of the quacks.

The Cambridge Scientific Instrument Company displayed an improved type of spectrometer freed from certain inaccuracies.

The Marine Biological Association exhibited dilute formic aldehyd used for the preservation of transparent organisms, a new method of fixing methylen-blue preparations, as devised by Prof. Bath, of Berlin.

Mr. Francis Galton, F.R.S., &c., displayed enlarged finger-prints, serving for identifying suspected criminals.

Prof. V. B. Lewes exhibited the preparation of acetylene from calcium carbide, and its combustion for illuminating purposes.

Major Cardew exhibited specimens which have of late been the subject of discussion in connection with street-explosions. The deposits shown contained metallic sodium and potassium liberated electrolytically.

A most interesting exhibit by W. T. Burgess proves the reality of the transmission of infection, *i. e.*, of pathogenic microbia, by flies.

Prof. Gotch, F.R.S., and Dr. H. O. Forbes exhibited a living specimen of the *Malapterurus electricus*, from the River Senegal.

Prof. A. Liversidge, F.R.S., of Sydney, exhibited gold nuggets, etched so as to show their crystalline structure. The designs obtained closely resembled the well-known Widmanstatt figures as shown by most metallic meteorites.

PHYSICAL SOCIETY.

Ordinary Meeting, April 26th, 1895.

Mr. Walter Baily, Vice-President, in the Chair.

Prof. S. P. Thompson read a note on "*A Neglected Experiment of Ampère.*"

Ampère, in 1822, made an experiment which, if it had been properly followed up, must have led to the discovery of the induction of electric currents nearly ten years before the publication of Faraday's results. While attempting to discover the presence of an electric current in a conductor placed in the neighbourhood of another conductor in which an electric current was flowing, Ampère made the following experiment:—A coil of insulated copper strip was fixed with its plane vertical, and a copper ring was suspended by a fine metal wire so as to be concentric with the coil and to lie in the same plane. A bar magnet was so placed that if an electric current was induced in the suspended ring a deflection would be produced. No such deflection, however, was observed.

In 1822, in conjunction with De la Rive, Ampère repeated this experiment, using, in place of the bar magnet, a powerful horse-shoe magnet. He describes the result in the following words:—"The closed circuit under the influence of the current in the coil, but without any connection with this latter, was attracted and repelled alternately by the magnet, and this experiment would, consequently, leave no doubt as to the production of currents of electricity by induction if one had not suspected the presence of a small quantity of iron in the copper of which the ring was formed." This closing remark shows that they were looking for a permanent deflection. When, however, Faraday's results were published in 1831, Ampère, after again describing the experiment made in 1822 by himself and De la Rive, says:—"As soon as we connected a battery to the terminals of the conductor, the ring was attracted or repelled by the magnet, according to the pole that was within the ring, which showed the existence of an electric current produced by the influence of the current in the conducting wire.

Verdet, when describing the above experiment, falls into a curious error. He says the apparatus consisted of a ring of fine copper wire, suspended by a silk thread in front of the pole of an electro-magnet, in such a way that the plane of the ring was parallel to the plane of the turns of wire on the electro-magnet. On "making" the current the ring is said to have been repelled, but this deviation did not persist; and on "breaking" the current the ring was attracted, also only momentarily.

Mr. Blakesley did not feel quite confident that in Verdet's form of the experiment there could ever be attraction. He also pointed out that, with an alternating current, the disc would tend to set itself parallel to the lines of force of the electro-magnet. With reference to repulsion by alternating currents, in one of Elihu Thompson's experiments, where a sphere is supported over an alternating pole, a screen being placed so as to partly shield this sphere, there is generally a misstatement as to the direction in which the sphere rotates. It rotates in such a direction that the part of the surface next the magnet moves towards the edge of the screen.

Dr. Burton said that, from the fact that when the current in the electro-magnet in Verdet's experiment is broken the induced current in the ring is in the same direction as the current in the magnet, the ring will be attracted.

Mr. Boys confirmed Dr. Burton's statement. He recommended setting the ring at an angle of 45° to the lines of force, under which circumstances a rotation would be obtained. A distinction must, he pointed out, be drawn between such an experiment as that of Verdet and those of Elihu Thompson. The repulsions observed in these latter were only due to the "lag" in the induced currents caused by self-induction. The best materials to use for all such experiments were magnesium and aluminium, since for a given mass these had the highest conductivity.

Mr. W. G. Rhodes read a paper entitled "*A Theory of the Synchronous Motor.*"

The object of this paper is to give as simple a treatment as possible of the mathematical part of the subject, and to give theoretical proofs of some experimental facts. Starting from the energy equation,—

$$p + c^2R = CE \cos \psi,$$

where p is the output of the motor, R the resistance of the armature, c the current through the armature, E the E.M.F. applied to the motor terminals, and ψ the phase difference between c and E, the cases of maximum output, zero output, minimum current at zero power, and maximum phase difference between c and E are considered. These results are, for the most part, obtained directly from the energy equation. The latter part of the paper is devoted to a discussion of the phase relationships between the current and the E.M.F.'s in a plant consisting of a generator and motor, and to the variations in the armature reactions in both generator and motor. A theoretical proof is given of the fact, observed by Prof. Silvanus Thompson and others, that an over-excited synchronous motor acts as a condenser, and tends to make the current lead before the generator's E.M.F.

Prof. S. P. Thompson said that the mathematical part of the paper was much simpler than that in previous investigations on this subject, and the method of arriving at the results by rejecting imaginary roots of the equations was particularly neat and instructive. The part of the paper relating to armature reactions and phase relationships was quite new. Two results deserved special attention; first, that the maximum current of zero power was the same as if the circuit was non-inductive; second, that the maximum current at zero power was double the current corresponding to maximum output.

Mr. Blakesley said that the paper did not consider the stability of the system, and he thought some of the results corresponded to regions of unstability.

A paper by Mr. Bryan, "*On a Simple Graphical Interpretation of the Determinantal Relation of Dynamics*," was, in the absence of the author, read by Dr. Burton.

The relation is worked out for two specially simple systems possessing one degree of freedom: (1) a particle moving in a straight line with uniform acceleration; (2) a particle moving to and fro along a straight line with an acceleration directed towards a fixed point on the line, and proportional to the distance from that point (simple harmonic motion). On constructing a diagram in which the abscissæ represent values of the single coordinate of the particle, and the ordinates corresponding values of the momentum, the determinantal relation becomes equivalent to the constancy of the area of a certain elementary parallelogram. In case (1) this parallelogram moves along a parabola, experiencing a shear as it goes; while in case (2) there is no distortion, the (rectangular) parallelogram revolving about the origin of the diagram as if rigidly attached to an inextensible radius vector.

NOTICES OF BOOKS.

Addresses in Commemoration of Josiah Parsons Cooke, LL.D., Late President of the American Academy of Arts and Sciences. Delivered at the Meeting of the Academy December 12th, 1894. (Extracted from the *Proceedings*, vol. xxx.). Cambridge (U.S.A.): J. Wilson and Son, University Press.

A considerable part of this pamphlet is worthily taken up with a biographical notice of the deceased, who will be endeared to all true followers of Science by the successful energy with which, in addition to his valuable researches in professional duties, he fought for the recognition of chemistry as a subject not less valuable than the "humanities" intrenched behind centuries of tradition. Chemical teaching at Harvard College had become extinct, and Cooke had to re-establish it. It is remarked that, like Liebig, "he had neither taste nor aptitude for the dead languages, and it was only with much difficulty that he surmounted the barrier of Greek and Latin which guarded the approach to Harvard College."

This is additional evidence—if any such is still needed—how little proficiency in "classics" can be regarded as a gauge for the intellectual power of a youth. It took Cooke "seven years of hard fighting to get chemistry adopted by the College as anything but an extra." He had by degrees to eliminate "recitations"—we presume committing a text-book to memory—in favour of the laboratory method devised by Liebig and taken up by Wœhler. It is remarked, drily, that neither of Cooke's earlier books ("Chemical Physics" and "Chemical Physiology") was popular with the students. They could not be, as they obliged their readers to think, and there is no occupation more distasteful to an undergraduate.

As an instance of the imperfect equipment of the institutions of higher education, we learn that "there was neither gas nor running water in University Hall, and Mr. Cooke's nearest neighbour, on the adjoining corner of the basement, was a baker's oven, where considerable batches of bread were baked every morning and evening, and yeast was sold every afternoon. A pump in the cellar yielded water for both bakery and laboratory, and within 50 feet of the pump was a privy which served for the whole college! Surely any comment on such a state of things could only be an anti-climax. It was a very fortunate circumstance that Prof. Cooke had inherited wealth, and was consequently not brought to a stand-still by the parsimonious conduct of the governing body of the College. He often supplied the laboratory of the lecture-room, at his own expense, with costly pieces of apparatus. Nor was he exposed to the painful necessity of spending his time on analytical or consultation work. A characteristic feature in his conduct was the readiness with which he appreciated and took up any new discovery. He devised improvements in the spectroscope, and constructed the most powerful instrument of his day. Several of his papers owe their origin to his work in spectrum analysis. He made a careful and enthusiastic study of the radiometer, which he regarded as a fresh evidence of the existence of a molecular universe. He was a zealous and successful photographer.

Prof. Cooke deserves, in short, the utmost honour as a man who would not endure the attempts of the "poor humanist" to relegate Science to a position of inferiority, and to force "longs and shorts and gerund-grinding" upon minds who crave for a different pabulum. At the same time he regarded Science as an essential element in a truly liberal culture, and was free from the narrow utilitarianism which so many persons confound with or prefer to the quest of truth for its own sake.

Qualitative Chemical Analysis of Inorganic Substances, as Practised in Georgetown College, D.C. By Rev. H. T. B. Tarr and Rev. J. W. Fox. New York, Cincinnati, and Chicago: American Book Company.

This book, being chiefly based upon the recognised text-books of Fresenius and Watts, may be expected to prove trustworthy, as in fact it really is. The only point on which we should beg to differ from the authors is in the composition of magnesia mixture.

The authors use magnesium sulphate, which we find less satisfactory than the corresponding chloride. But, as a general principle, we dislike any analytical manual which omits the rarer elements. Such substances may at any time occur in natural minerals, or in artificial compounds and mixtures, and may modify the reactions which the student has been taught to expect. It is possible that in America the chemical public has not yet been so supersaturated with manuals, "manualettes," and handbooks, as has been the case in Britain.

We find here no reference to any syllabus, or to any examination for which the student has to prepare. This is a point which deserves our thankful acknowledgment.

The Pharmaceutical Journal of Australasia. Vol. viii., No. 2.

This Journal is less—much less—a scientific than a trade organ. There is an account of the position and prospects of Fremantle, and of Western Australia in general, not calculated to attract pharmacists or indeed settlers of any kind. Quacks, calling themselves "specialists," seem to be watchful and alert in the Colonies, and will need careful looking after.

The New Zealand Colonial Government has offered a prize of £1000 for the first 200 tons of crude potassium cyanide manufactured from local produce. Nitrogenous refuse suitable for this manufacture ought to be abundant, but we fear the Colonies—or indeed the entire Empire—will not supply the potash. But has a sufficient search been made?

We are happy to learn that the cultivation of perfume plants is being pushed forward at Dunelly. The temperature in South Australia (indoors) ranges from 90° to 98°,—a set-off, we presume, to the arctic weather with which the home-kingdoms have been afflicted.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 16, April 22, 1895.

New Deposit of Uranium.—Baron Nordenskiold.—I have not yet completed my researches on the uraniferous minerals. I believe I have this winter discovered a very important deposit of uranium. It is certain sedimentary beds of a carboniferous composition the ash of which yields from 2 to 3 per cent of uranium. This uraniferous substance contains also some nickel and rare earths and a considerable quantity of nitrogen. Perhaps it may also contain an abundant source of argon or of helium.—(*Extract from a letter from Baron Nordenskiold to M. Daubrée.*

Crystals Forming at the Bottom of a Solution Heavier than Themselves.—Lecoq de Boisbaudran.—On p. 539 of the present volume the author has described crystals forming on the surface of liquids lighter than themselves. He now has observed an inverse phenomenon in the case of sodium sulphate with 10 per cent Aq. He takes a solution of sodium iodide, saturated with sodium sulphate, and of a density a little greater than that of the crystals of sodium sulphate with 10 Aq. The crystals at first float upon the surface, but after a few days subside to the bottom.

Specific Heat and Boiling-point of Carbon.—J. Violle.—Above 1000° the mean specific heat of graphite increases in a linear manner with the temperature according to the formula—

$$C_0^t = 0{\cdot}355 + 0{\cdot}00006\,t.$$

The temperature of ebullition of carbon is 3600°.

On Photography in Natural Colours by the Indirect Method.—Aug. and Louis Lumière.—The authors obtain successively on the same plate three monochromes, red, yellow, and blue, from three corresponding negatives, using the precaution to isolate each image from the foregoing by an impenetrable layer, *e.g.*, collodion.

Molecular Rotation and Molecular Deviation.—Ph. A. Guye.—The author remarks that there are two manners of conceiving the mean deviation due to the action of an active molecule: the molecular rotation which supposes all the liquids brought to the same volume containing the same number of molecules and examined with the planimeter is one and the same thickness; the molecular deviation when we suppose all the active liquids examined with the polarimeter in depths such that the polarised ray always meets in its course the same number of active molecules in the direction of the length of the active medium.

Certain Derivatives of Quinone-di-ortho-amino-benzoic Acid.—J. Ville and Ch. Astre.—The action of reducing agents and of benzoyl chloride upon the above acid reveals in this compound the persistence of the quinonic function. On the other hand, the researches of Knapp on the chloroquinones (*Berichte*, xiv., p. 1233) show that the products obtained with the primary amines must be considered as derived from the quinones by the substitution of two groups (NHR')' for two hydrogens.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 108.

This number contains no chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 3, 1895.

At the meeting on January 11 the financial report of the Society for the past year was presented. It was accepted by acclamation, and a silver medal, bearing the likeness of Lavoisier, was voted to the retiring President, A. Scheurer-Kestner.

The staff and Council for the present year will be:—

President—Maquenne.

Vice-Presidents—Moissan, Wyrouboff, Béchamp, and Suilliot.

Secretaries—Béhal and Verneuil.

Vice-Secretariees—Bigot and Lindet.

Treasurer—Petit.

Achivarian—Clöez.

Other Members of Council—Le Bel, André, Tanret, Riban, Friedel, Schützenberger, A. Combes, Hanriot, Scheurer-Kestner, Engel, Adrian, and Joly.

The non-resident members of Council are Péchiney, Buisine, Haller, and Barbier.

The President announced that he had received official information that the Congress of learned societies will be held at the Sorbonne, on April 16, at 2 p.m.

During the month of December, 1894, the Society took charge of three "sealed papers."

Project of Nomenclature of some Stereo-Chemical Isomers.—R. Lespieau.—The author's proposal cannot be explained without the insertion of a number of formulæ which are, in fact, diagrams.

On the Acid Potassium and Silver Fluorides.—M. Guntz.—A thermo-chemical paper. The author determines the formation-heats of the acid fluorides discovered by Moissan.

Certain Thiohypophosphates.—L. Ferrand.—The author has obtained and determined the thiohypophosphates of zinc, $P_2S_6Zn_2$, the corresponding cadmium salt, $P_2S_6Cd_2$, and the nickel salt, $P_2S_6Ni_2$.

Action of Chlorine upon the Secondary Alcohols.—A. Brochet.—The action of chlorine upon the secondary alcohols of the form $R.CHOH.CH_3$ gives chloro-acetones of the form $R.CO.C'Cl_3$.

Certain Glycerins derived from the Secondary Allylic Alcohols.—H. Fournier.—An examination of the glycerin of ethylallylcarbinol, of its triacetine, of the glycerin of isopropylallylcarbinol triacetine, of the glycerin of isobutylallylcarbinol, and that of phenylallylcarbinol.

Nitrosopropylacetamide.—F. Chancel.—This substance is mobile, of a rose colour if seen in a thick stratum, but yellow in slender layers, as is its aqueous solution. Its sp. gr. at 15° is near that of water, 1·035.

Presence of Glyoxylic Acid in Green Fruits.—H. Brunner and E. Chuard.—The authors reject the view of Ordonneau that the acid in question is the tartaro-malic. They have also recognised the presence of formic acid along with the glyoxylic and glycolic acids.

Researches on the Constitution of Hexamethyleneamine.—M. Delépine.

Hydrogenation of Hexamethyleneamine. Formation of Trimethylamine.—M. Delépine.—This paper, like the foregoing, does not admit of useful abstraction.

Essence of Cananga.—A. Reychler.—In a general manner the qualitative resemblance of the oil of ylang-ylang and that of cananga is so complete that it cannot be accidental. It is possible that the two essences are obtained from the same vegetable species.

Detection and Separation of Free Hydrochloric Acid and of Chlorides. Application to the Analysis of the Gastric Juice.—H. Lescoeur.—This paper will be inserted at some length.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Society of Arts, 8. (Cantor Lectures). "Recent American Methods and Appliances employed in the Metallurgy of Copper, Lead, Gold, and Silver," by James Douglas.
— Medical, 8. (General Meeting).
TUESDAY, 14th.—Royal Institution, 3. "Thirty Years' Progress in Biological Science," by Prof. E. Ray Lankester, F.R.S.
— Institute of Civil Engineers, 8.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
WEDNESDAY, 15th.—Society of Arts, 8. "Means for Mitigating the Fading of Pigments," by Captain W. de W. Abney, F.R.S.
— Microscopical, 8.
— Meteorological, 7.30.
THURSDAY, 16th.—Royal, 4 30.
— Royal Institution, 3. "The Liquefaction of Gases," by Prof. Dewar, F.R.S.
— Chemical, 8. Ballot for the Election of Fellows. "Kjeldahl's Process for the Determination of Nitrogen," by Dr. Bernard Dyer. "The Action of Nitrous Acid on 1 : 4 : 2 Dibromaniline," by Prof. Meldola, F.R.S., and E. R. Andrews. "Derivatives of Succinyl and Phthalyl Dithiocarbimides," by Prof. Dixon and Dr. Doran.
FRIDAY, 17th.—Royal Institution, 9. "Robert Louis Stevenson," by Prof. Walter Raleigh.
— Quekett Club, 8.
SATURDAY, 18th.—Royal Institution, 3. "Picture Making," by Seymour Lucas, A.R.A.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1851.

THE POSITION OF ARGON IN THE PERIODIC SYSTEM.

By W. W. ANDREWS.

I have been engaged in projecting the curves of atomic volume, melting-point, &c., into the vacant space between hydrogen and lithium, to see if, with corrected values, the Periodic Law can be made the instrument for prophecy, as in the cases of Sc, Ge, and Ga. The regularities of the curves show this, that the members of the second and third families, supra-beryllium and supra-boron, should have properties similar to argon, the former especially.

In the lower series, the neutral element is found in the fifth and sixth families, in the third between Al and Si, in the second at boron, and in the first it should be at supra-beryllium.

Not only so, the atomic volume curve should descend from H as it does from Li, Na, K, Rb, &c., and should rise at supra-nitrogen and supra-oxygen. If we take the value obtained from its alloys the atomic volume of H is

$$\frac{1}{0\cdot 63} = 1\cdot 587\,;$$

supra-Be should then be less than unity. The atomic weight of an element for that position should be about 1·5 or 1·6, and the density of argon is 1·5, perhaps 1·7 or 1·8 as a solid; these values give a value for atomic volume of the required dimensions.

But small atomic volume is the condition of polymerisation, or, rather, both spring from some common condition, great inter-atomic attractions. Great chemical inertness accompanies both of these. We may expect from the very small atomic volume less than unity, great attraction of supra-beryllium atoms for like atoms, and therefore little susceptibility to attack from other elements, and as the atomic volume is less than unity, several atoms would be crowded into the same *atomic* space—a new condition in gas chemistry. Would a polymerisation of a grade represented by the fraction—

$$\frac{40}{1\cdot 5} = \frac{\text{seeming atomic weight of A}}{\text{atomic weight of supra-Be}} = 28$$

or thereabouts be too much to expect? Would not such a group of atoms act like single atoms, or the ordinary elementary molecules? Should it not also be expected to act like a perfectly round body, and therefore give the ratios between the specific heats exhibited by argon? Its spectrum should be like those found at the alkaline end of Lothar Meyer's table, and such I see is the case.

The melting point curve should rise rapidly from hydrogen to supra-carbon. Hydrogen should solidify at $-243+x$, perhaps -250 or -260. Argon, then, drops in the place of supra-Be in this curve also.

I am anxious to know its refraction-equivalent, and will wait with interest future developments. Berthelot, I see, reports an alkaline reaction from the new argon compound.

If the next few months bring the requisite facts, I shall have all my curves accurately drawn in a form ready for publication. The curves of atomic volume, melting-points, of acid and alkaline power, if projected from Cs, Ba, La, and Ce over the vacant space to Os, Ir, Pt, Au, &c., and again over vacancy to Th and U, are such that these elements drop into their places in the three curves, and thus the whole is found to be one system. We ought to be able to prolong the curves into Series I. to hydrogen, though on account of the tendency to greater accentuation of difference, the task is one of greater difficulty.

Let us imitate the sublime faith of Mendeleeff, and we may rest assured that the order and multiplied analogies revealed by the Periodic Classification form a basis of fact which is not to be shaken. Argon and helium will drop into their places and open up new vistas of analogy and suggestion.

Science Laboratory, Mt. Allison University,
Sackville, N.B., Canada, April 29, 1895.

VOLUMETRIC DETERMINATION OF SUGAR BY AMMONIO-CUPRIC SOLUTION.*

By ZDENEK PESKA.

Of the various methods propounded for the quantitative determination of sugars, three have found favour in the eyes of chemists—the original Fehling titration, the improved Soxhlet process, and the Soxhlet-Allihn gravimetric method. The latter is most frequently employed, but occasionally, when speed is more important than minute accuracy, the old Fehling process is still used.

The gravimetric method is, however, not always free from serious faults. For instance, personal experience has shown that various kinds of asbestos are not unaffected by the alkaline-copper solution, the filter itself losing weight, according as the operation is performed rapidly or slowly. Hence the only method which can lay claim to accuracy is the Soxhlet titration, but this unfortunately requires such a long time for its performance that it is seldom used, and is also open to objection in that where ammonia compounds are present in the sugar solution some of the cuprous oxide dissolves, and a copper reaction may be detected in the filtrate. This circumstance may, however, be utilised in quantitative estimations of sugar. If an excess of ammonia be added to the Fehling solution the cuprous oxide remains dissolved, the deep blue liquid containing ammonio-cupric salts being reduced, by a sufficient quantity of sugar, to a colourless solution of ammonio-cuprous compounds.

This idea was utilised by Pavy (Chemical News, xxxix., 77), who added a large excess of ammonia to the Fehling solution and treated the boiling liquid with sugar solution until decolouration was effected. Ammonia was evolved on boiling, and Pavy relied on this to ensure the exclusion of air necessary to prevent the re-oxidation of the cuprous solution. It will be readily understood that this procedure can only effect an incomplete exclusion of air, and that the proportion of alkali in the solution—which influences the reducing power of the sugars—does not remain constant when the liquid is boiled.

Attempts made to totally exclude the air by means of a gentle current of hydrogen passing through the reacting liquid in a flask did not succeed. In the first place, the removal of the final traces of air from the generating flask and washing apparatus was very tedious; and, secondly, the hydrogen carried away a portion of the ammonia from the solution, thus perpetuating the second error previously referred to.

However, by employing, instead of an indifferent gas, an inert liquid of lower specific gravity than the solution, the work can be carried out satisfactorily, and for this purpose *pure paraffin oil* is particularly suitable. If the Fehling solution mixed with ammonia be covered with a layer of about 0·5 c.m. of paraffin oil, not only is contact with air cut off, but the escape of ammonia is prevented, and constancy in the proportions of the solution ensured.

The added ammonia must be sufficient in quantity to maintain the cuprous oxide in solution, but not so large

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* " Vorlaüfige Mittheilung aus den Abhandlungen der böhmischen Akademie der Wissenschaften " (through *Zeitschrift fur Rübenzucker-Industrie*, xxxiv., pp. 165—168).

as prescribed by Pavy, as an evolution of the gas will occur when heat is applied, which, by disturbing the oil layer, will facilitate the admission of air. The proportion experimentally ascertained as most suitable is 80 c.c. of 25 per cent liquid ammonia per 3·634 grms. of cupric sulphate; the reaction should not be carried out at boiling heat, but at lower temperature (80° to 85° C.).

At first ammonio-cupric solution was used equal to decinormal Fehling, but it being found that only very small amounts of sugar could be treated by this strength (a maximum of 0·044 grm. of glycose per 100 c.c. of copper solution), a solution twice as strong as the above was prepared and found satisfactory. A higher degree of concentration is not recommended on account of the large amount of ammonia requisite.

The solution employed is made up in two stages, as follows:—Dissolve 6·927 grms. of crystallised cupric sulphate in water, adding 160 c.c. of 25 per cent ammonia, and make up to 500 c.c. on cooling. Then dissolve 34·5 grms. of Seignette salt and 10 grms. of NaHO in water, making this solution also up to 500 c.c. when cool. Measure off exactly 50 c.c. of each, cover the mixture with the layer of oil, and add the sugar solution at 80° to 85°.

As was revealed by Soxhlet's researches, the reducing power of sugars depends, not only on the concentration of the alkaline copper solution, but also on the strength of the sugar solution, and the same is observable in the case of the present reagent.

100 c.c. of the weaker solution (= $\frac{1}{10}$ normal Fehling) required for its reduction 0·044 grm. of glycose in 0·5 per cent solution. The same quantity of the double strength solution took 0·0806 grm. of glycose (in 0·5 per cent solution) to produce decolourisation. Stronger solutions of glycose exert a more powerful reducing action, and *vice versa.* For instance, 100 c.c. of ammonio-cupric solution are reduced by 0·0801 grm. of 1 per cent glycose, while 0·0821 grm. is necessary in the case of a 0·1 per cent solution.

In order to make this process available for analytical work, tables had to be calculated showing the amount of sugar, in various degrees of dilution, required for the reduction of 100 c.c. of the reagent solution, regard being chiefly had to the behaviour of glycose, invert sugar, invert in presence of saccharose, milk sugar, and maltose.

A.—*Glycose.*

A pure preparation, repeatedly re-crystallised from methyl alcohol, was taken, and the determinations made with solutions from 1 per cent down to 0·1 per cent strength. The amount of glycose required for the reduction increases fairly regularly with the degree of dilution.

The following table shows the amounts in c.c. and m.grms. of glycose of various degrees of concentration required for the reduction of 100 c.c. of ammonio-cupric solution, and will give a regular curve, provided the highest degrees of concentration are excluded. The figures will be found suitable for use in analysis, omitting the second place of decimals, as the accuracy of the method does not extend so far.

TABLE I.

100 *c.c. of Ammonio-cupric Solution are Reduced by a Solution of Glycose.*

Percentage strength of glycose solution.	C.c. of glycose required.	= M.grms. of glycose.
1·0	8·02	80·20
0·9	8·90	80·10
0·8	10·03	80·24
0·7	11·47	80·29
0·6	13·40	80·40
0·5	16·12	80·60
0·4	20·20	80·80
0·3	27·05	81·15
0·2	40·80	81·60
0·1	82·10	82·10

B.—*Invert Sugar.*

This sugar was prepared, according to Soxhlet's method, from saccharose purified by re-crystallisation from alcohol, 9·5 grms. being dissolved in 500 c.c., and, after addition of 200 c.c. of decinormal hydrochloric acid, inverted for thirty minutes on the water-bath, and finally made up to 1000 c.c. when cooled.

This, diluted to the same degree as the glycose solution, displayed, on testing, a reducing effect having a ratio of 94·9 : 100 as compared with the latter, their behaviour being similar.

TABLE II.

100 *c.c. of Ammonio-cupric Solution are Reduced by Invert Sugar Solution.*

Percentage strength of invert solution.	C.c. of invert sugar consumed	= M.grms. of invert sugar.
1·0	8·40	84·00
0·9	9·37	84·33
0·8	10·55	84·40
0·7	12·07	84·49
0·6	14·12	84·72
0·5	17·03	85·15
0·4	21·33	85·32
0·3	28·63	85·89
0·2	43·25	86·50
0·1	87·03	87·03

C.—*Invert Sugar in presence of Saccharose.*

In order to test the influence of saccharose on the reagent solution three series of experiments were made with 0·2, 0·5, and 0·8 per cent solutions of invert, containing varying amounts of saccharose, from 1 to 30 grms. per 100 c.c. The results showed the reducing power of saccharose to be extremely weak, 1 grm. of saccharose only producing the same effect as 0·0023 grm. of invert.

Application of the Test.

One preliminary experiment and two exact determinations are necessary, proceeding as follows:—

Measure into a dry beaker 50 c.c. of the ammonio-cupric solution from a burette, to which add from a pipette 50 c.c. of the alkaline Seignette solution, so that all the copper is washed off the sides of the glass, and immediately cover the liquid with a layer of pure paraffin oil about 0·5 c.m. deep. Heat the liquid carefully over wire gauze up to 80°—measured by the thermometer serving as a stirring-rod—and run in down the side of the vessel the sugar solution out of a Geissler burette tapped in front, so that the burette itself may stand on one side and be shielded from the heat of the flame by a sheet of asbestos. The sugar is added by c.c., the mixture being carefully stirred between whiles, and the temperature should be between 80° and 85°. Arrived at the point when the addition of 1 c.c. decolourises the liquid, the second experiment is proceeded with. This consists in an exact repetition of the first, except that the sugar is run in at once, and that 1 c.c. less of sugar is taken, so that the liquid remains blue. Now push the beaker away from the point of the burette and wash down the sugar on the side of the glass with 10 drops of water from a pipette. Then bring the temperature up to 85° again in two minutes, and continue adding the sugar by $\frac{1}{10}$ths of a c.c., with gentle stirring, until the colour disappears. As, notwithstanding the oil layer, the liquid gradually oxidises, the whole reaction, from the first addition of the sugar until complete decolourisation, should be carried out in five minutes.

The third test is a check repetition of the second.

The author cites typical analyses showing the concordant results obtained by his method.

Appointment.—Mr. Leo Taylor, F.I.C., F.C.S., has been appointed Public Analyst for Hackney, in succession to the late Dr. Tripe.

VARIATION IN THE AMOUNT OF FREE AND ALBUMENOID AMMONIA IN WATERS, ON KEEPING.

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

(Continued from p. 226).

Table IV.

Five Bottles each, Urine and Horse Pond Waters.

Temp. °F. Morn.	Temp. °F. Ev.	Nos.	Date.	Horse Pond. Free NH_3.	Horse Pond. Alb. NH_3.	Urine and Distilled Water. Free NH_3.	Urine and Distilled Water. Alb. NH_3.
70	72	1	Nov. 3	0·35	0·08	0·09	0·012
74	76	2	„ 7	0·20	0·08	0·18	0·12
74	76	3	„ 11	0·05	0·08	0·18	0·12
74	76	4	„ 13	0·05	0·08	0·19	0·11
75	75	5	„ 14	0·03	0·07	0·21	0·12

In all cases where mixtures gave such large amounts of ammonia as to be unworkable they were, at the time of mixing, diluted with the requisite quantity of distilled water to bring the ammonia down to working limits.

The second of the above series (urine and distilled water) did not contain enough bottles; the amount of free ammonia increased from 0·09 to 0·21 in 11 days; if the experiment had been carried on for a longer time a larger amount might have been set free.

Table V.

Five Bottles each, Urine and Horse Pond Water.

Temp. °F. Morn.	Temp. °F. Ev.	Nos.	Date.	Horse Pond and Garden Tank. Free NH_3.	Horse Pond and Garden Tank. Alb. NH_3.	Urine and Distilled Water. Free NH_3.	Urine and Distilled Water. Alb. NH_3.
76	76	1	Nov. 16	0·60	0·18	0·56	0·56
72	75	2	„ 21	0·01	0·13	1·20	0·39
74	76	3	„ 22	0·01	0·13	1·28	0·35
72	72	4	„ 24	0·01	0·11	2·56	0·29
66	69	5	„ 27	0·01	0·11	1·60	0·32

Note.—Rain on Nov. 11th.

In the second series containing urine the gradual increase and then decrease of free ammonia is very marked, the decrease of albumenoid ammonia going on very regularly.

Table VI.

Twelve Bottles Garden Tank Water and Urine.

Temp. °F. Morn.	Temp. °F. Even.	Nos.	Date.	Free NH_3.	Alb. NH_3.
72	72	1	Nov. 24	0·27	0·27
66	69	2	„ 27	0·32	0·18
66	68	3	„ 29	0·20	0·18
67	68	4	„ 30	0·20	0·18
68	68	5	Dec. 1	0·16	0·15
66	71	6	„ 4	0·28	0·36
73	73	7	„ 6	0·36	0·40
76	77	8	„ 7	0·24	0·27
77	78	9	„ 8	0·17	0·15
73·5	75	10	„ 11	0·16	0·14
77	76	11	„ 12	0·14	0·13
71·5	72	12	„ 13	0·13	0·10

Note.—No rain from Nov. 11th.

If only the last two bottles of the above had been examined the impression conveyed would have been very different to that from the earlier and intermediate ones. Hence a very seriously contaminated water (were the ammonia tests solely relied upon) might, if kept for a few weeks, be passed as a fair or even good water.

(To be continued).

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* Read before the Australasian Association for the Advancement of Science, Brisbane, January, 1895.

ON DEXTROSEBENZHYDRAZIDE.

By HEINRICH WOLFF.

Some time ago Herzfield and the author, and subsequently the author alone, had reported on the combination of dextrose and amidoguanidine, and in the meantime the author has obtained the compounds of amidoguanidine with galactose and lactose, on which I shall in future report in full. Although these compounds crystallise beautifully they are very soluble in water, and hence not suitable for separating the aldoses from other sugars. Now amidoguanidine may be regarded also as hydrazine, in which an atom of hydrogen of the diamide is replaced by the guanidine complex, that is, as guanidine hydrazine. It seemed therefore probable that also the hydrazides in which a hydrogen atom of the hydrazine is substituted by an acid residue should react with the aldoses, especially as phenylhydrazine also reacts.

The first compound of this kind, arabinosenitrobenzhydrazide, was obtained by Redenhausen at the instigation of Herzfeld, whilst the writer obtained dextrosebenzenesulphonhydrazide and dextrosebenzhydrazide.

Benzhydrazide was first produced by G. Struve, a pnpil of Curtius.

The reaction between the aldoses and the acidylhydrazides ensues according to the following equation:—

$$\begin{aligned}&R:C:O.NH.NH_2+O:C.H.R.=\\&=R.C.O.N.H.N:C.H.R+H_2O.\end{aligned}$$

The production is effected as follows:—The finely-powdered aldose and the hydrazide, the latter in slight excess, are introduced into an Erlenmeyer flask, covered with alcohol at 96 per cent, and heated five or six hours in the reflux refrigerator. If sufficient alcohol has been taken the whole dissolves, but if the alcohol is insufficient the compound formed is re-precipitated, and the liquid begins to bump. We then evaporate nearly to dryness on the water-bath, when the whole congeals to a paste of fine needles, which subsequently becomes solid. If the reaction has not been completed on boiling, it is hereby brought to an end, and it is allowed to cool, when the substance separates out in fine needles, which are filtered off and are re-crystallised from alcohol.

Dextrosebenzenesulphonhydrazide.—This compound is formed according to the equation—

$$\begin{aligned}&C_6H_5SO_2NH.NH_2+C_6H_{12}O_6=\\&=C_6H_5SO_2NH.N:C_6H_{12}O_5+H_2O.\end{aligned}$$

It is prepared in the manner indicated. Its composition is $C_{12}H_{18}N_2O_7S$. It separates from alcohol in white needles, which melt at 154° to 155°, with a brown colour and decomposition. In cold water it is rather sparingly soluble, and can be re-crystallised from water in the form of small rhombic crystals, which form crusts; but the temperature must not exceed 70°; as soon as bubbles of gas rise out of the liquid, decomposition sets in. The substance is lævo-rotatory, moderately soluble in hot alcohol, sparingly in cold alcohol, insoluble in ether.

Dextrosebenzhydrazide is formed from dextrose and benzhydrazide, according to the equation—

$$C_7H_8N_2O+C_6H_{12}O_6=C_{13}H_{18}N_2O_6+H_2O.$$

Its composition is $C_{13}H_{18}N_2O_6$. Crystallises from alcohol in white needles, which melt with decomposition at 171° to 172°, turning brown. Its conditions of solubility are almost the same as those of the benzenesulphonehydrazide compound, and it is also lævo-rotatory.

Scission of Dextrosebenzhydrazide.—If this compound is boiled in water it is split up smoothly into dextrose and benzhydrazide, as mentioned by Radenhausen. If benzaldehyd is added, drop by drop, insoluble benzalbenzhydrazide is at once precipitated. It is convenient to proceed as follows:—Dextrosebenzhydrazide is dissolved in hot water in an Erlenmeyer flask, the calculated quantity of benzaldehyd is added, and the whole is boiled for about five minutes with constant agitation. It is then allowed to cool, the benzalbenzhydrazide is sucked off, and the filtrate is again boiled with the addition of a little benzaldehyd to ascertain if the reaction is complete. The filtrate is evaporated to dryness, taken up with a little cold water in order to remove traces of benzalbenzhydrazide, evaporated again, taken up with alcohol, and precipitated with either to remove benzaldehyd and benzoic acid, repeating the operation if necessary. The dextrose is then quite pure.

The cause of the scission may be most readily seen in dextrosebenzenesulphonhydrazide. If, namely, benzenesulphonhydrazide alone is heated in water, the following reaction occurs :—

$$2C_6H_5SO_2NH.NH_2 = C_6H_5.SO_2.N.H,NH.SO_2.C_6H_5 + \\ + N_2.H_4.$$

A single ebullition is sufficient to produce this result. Hence if dextrosebenzenesulphonhydrazine is evaporated down with water, the following reaction takes place :—

$$2C_6H_{12}O_5.N.NH:SO_2C_6H_5 + 2H_2O = \\ = 2C_6H_{12}O_6 + 2N:H_2.NH.SO_2C_6H_5.$$

The latter, as above stated, forms at once dibenzenesulphonhydrazide (with a violent escape of gas), and behaves with the sugar like a strong acid.

As the benzhydrazide passes into dibenzhydrazide only at a high temperature, we may perhaps assume that the tendency to this change is the primary cause of the scission.—*Berichte*, xxviii., No. 2, p. 160.

THE DETECTION OF BLOOD-SPOTS, ESPECIALLY IN PRESENCE OF RUST.

By Herren MECKE and WIMMER.

The authors recommend the observation of the absorption spectrum of oxyhæmoglobine in the following manner :—

Some particles of a spot occurring on iron are placed on a port-object, touched with a small drop of water, and heated for a short time to about 30°, replacing the water as it evaporated. If the spot was old and dried up in a thin layer, the chief part of the colouring-matter of the blood is oxidised to methæmoglobine. In order to reconvert it into oxyhæmoglobine they add to the solution on the port-object a trace of a solution of tartaric acid, ferrous sulphate, and excess of ammonia, by means of a glass rod drawn out to a fine point. Along with the drop they lay on the port-object a horse-hair, and over all a covering-glass. By cautiously raising the superimposed corner the drop of liquid is moved to the middle of the covering-glass, under which a second horse-hair is pushed. The drop now forms a minute column between the port-object and the covering-glass, the depth of which needs to be merely 1 m.m. in order to obtain an observation of the absorption-spectrum. In this manner we may operate with 0·5 cubic millimetre, or only 0·0005 grm. of liquid. If no micro-spectrum apparatus is available, the edges of the covering-glass are fixed to the port-object with melted wax or paraffin, the eye-piece and the illuminating arrangement are removed, and the microscope is placed in a horizontal position. The spectroscope is set in front of the microscope in such a manner that the tube of the latter lies in a straight line with the slit-tube of the former, the object is illuminated in a suitable manner, and the absorption-spectrum is examined.

If the stains are dried upon cloth it is digested in water, the liquid is evaporated down to a small volume, and a trace of ammonium sulphide is added, which effects the transformation of methæmoglobine more speedily. This reagent is not applicable in presence of rust, in consequence of the formation of iron sulphide.

Less sharp spectra are obtained after drying up the solution of blood upon some fibres of linen or white silk, laid close together and moistened with glycerin containing ammonium sulphide, covered with a covering-glass, and then examined with the micro-spectroscope.

The reduction-liquids must in all cases be added cautiously, to prevent the formation of hæmoglobine, the absorption-band of which is not so distinct as the absorption-bands of oxyhæmoglobine.

If suspicious spots are found on articles of iron, solution in hydrochloric acid often gives a clue to their nature. If a few particles of the substance in question are heated on the port-object with hydrochloric acid, the solution contains flocks if blood is present.

The guaiacum test for blood has been recently recommended by Schär. He pronounces a spectroscopic examination, and the production of crystals of hæmin, the most certain methods, and indispensable in the conduct of forensic investigations, but the guaiacum test is still valuable.

It has been urged as an objection that nitrous acid and other oxidising agents turn the tincture of guaiacum blue; but these substances react *without* an addition of oil of turpentine, and are thus sufficiently distinguished from blood. The latter (and also hæmatine) transfer oxygen from ozonised blood to guaiacum resin, thus rendering its constituent guaiaconic acid blue. This property (of acting as a transferrer of ozone) is shared by blood after it has been heated to about 100°; it is therefore not dependent on any ferment present in blood.

For the detection of small quantities of blood Schär mixes the aqueous liquid in question with tincture of guaiacum, and filters. This tincture consists of 1 grm. of the resin in 100 c.c. of absolute alcohol. There remains on the filter finely-divided resin along with constituents of blood, if blood was present. The filter is then shaken up in Hänefeld's mixture (consisting of oil of turpentine, alcohol, and chloroform, 200 parts of each; glacial acetic acid and water, 2 parts of each). The presence of blood is shown by a blue colour. A negative result of this test proves the *absence* of blood, but a positive result is no certain demonstration of its presence. —*Zeitschrift fur Analyt. Chem.*, and *Pharm. Zeit.*

THE USE OF SODIUM PEROXIDE IN ANALYSIS.

By Herren HEMPEL, SPULLER, KALMAN, and POLECK.

This reagent, exceedingly rich in oxygen, is more suitable than any other substance for oxidations at a red-heat.

If we mix chromiferous or manganiferous substances with about twice their weight of the peroxide, and heat on sheet-silver or platinum, the mixture becomes almost immediately deep yellow or green. Tungsten mineral, if mixed with 4 parts of the peroxide, gives in a few minutes a melt from which sodium tungstate can be easily extracted on treatment with water.

Titaniferous iron ore can be opened up in a very short time by mixture with 4 parts of sodium peroxide, and fusion in a silver crucible. The melt is extracted with hot water; the precipitate, containing ferric oxide and the titanic acid, is placed without washing in a platinum crucible along with concentrated sulphuric acid, which is evaporated down to a slight residue. Hence we obtain all the titanic acid in solution if the liquid, when quite cold, is poured into a large quantity of cold water. If the solution is not perfectly clear it is filtered, and then the titanic acid is separated as usual by prolonged ebullition, with the introduction of sulphurous acid.

Sulphur compounds are oxidised with explosive violence. For determining sulphur Hempel uses, to 1 part of the substance in question, 2 parts soda and 4 parts of peroxide, and melts the mixture in a silver crucible. The chief part of the melt is conveniently poured into a capsule of silver, nickel, or platinum, standing in cold water. It is filtered, acidified with hydrochloric acid, and precipitated with barium chloride.

For the complete analysis of blende and galena it is also recommended to open up with sodium peroxide, since the iron is at once separated as oxide, whilst lead and zinc pass into the alkaline liquid.

J. Spuller and S. Kalman have also made experiments which lead to analytical methods. They have successfully oxidised with sodium peroxide ferrochrome, chrome-steels, chrome-iron ore, and sulphur ores.

The experiments of Poleck are also interesting. Whilst a great number of organic liquids—glacial acetic acid, benzaldehyd, ether, &c.—are at once ignited, ethylic alcohol behaves quite differently; substances dissolved in alcohol can be easily oxidised by sodium peroxide. Iodine was oxidised to periodic acid, lead to sodium orthoplumbate. On the other hand, salts of silver and mercury, as also potassium permanganate, were reduced.—*Zeit. fur Anorg. Chemie* and *Chemiker Zeitung*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Anniversary Meeting, April 25th, 1895.

Mr. A. G. **Vernon Harcourt**, President, in the Chair.

Messrs. Francis H. Carr, A. T. Cocking, Alexander Hogg, and Frank Newbolt were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edgar S. Barralet, 61, Thistlethwaite Road, Clapton, N.E.; Gustav Theodore Bruckmann, B.Sc., 192, 18th Street, Brooklyn, N.Y.; Walter W. Cheadle, B.A., 19, Portman Street, W.; Sydney Fawns, 16, Onslow Gardens, S.W.; Alexander F. Fuerst, Ph.D., 30, Belsize Road, N.W.; William Goddard, 11, Granville Road, Middlesbrough; Patrick Hope Grant, 57, S. Guildry Street, Elgin, N.B.; William Abraham Greaves, B.Sc., Bankside, Golden Valley, Alfreton; Charles Butterworth Newton, Gasworks, Rotherham; Frank L. Slocum, Pittsburgh, Pa.; Alfred Stanfield, B.Sc., 21, Markham Square, S.W.; William Thomas Thomson, Austin Villas, Station Road, Waltham Cross; Arthur Thornton, M.A., 67, St. Mary's Terrace, Manningham; William Arthur Whiston, Collegiate School, Llandudno; John Wilson, B.Sc., 11, Cupar Road, Battersea, S.W.

Of the following papers those marked * were read:—

*45. "*Action of Nitrosyl Chloride on Amides.*" By **William A. Tilden**, F.R.S., and **M. O. Forster**, Ph.D.

The authors find that the interaction of nitrosyl chloride and amides generally results in the exchange of the amidogen group, NH_2, for an atom of chlorine; but as a molecule of water is formed simultaneously, the chloride produced is converted into the corresponding acid more or less completely according to the conditions of the experiment. Acetamide, benzamide, malonamide, oxamic acid, urea, and urethane behave in this way.

Glycocine and asparagine, as examples of amido-compounds, give the corresponding chloro-acid.

Oxamide is entirely unaffected by nitrosyl chloride at any temperature up to 100°. Oxanilide, hippuric acid, succinimide, and phthalimide are also unattacked.

Since glycocine and asparagine (or aspartic acid) exchange NH_2 for Cl like the amides, the authors regard this as confirming the formulæ by which these substances are represented as amido-derivatives of acetic and succinic acids respectively. They consider the closed chain formulæ, lately revived by Sakurai, to be inadmissible.

*46. "*Action of Nitrosyl Chloride on Asparagine and Aspartic Acid; Formation of Lævorotatory Chlorosuccinic Acid.*" By **William A. Tilden**, F.R.S., and **B. M. C. Marshall**.

The authors have studied the products of the action of nitrosyl chloride on asparagine dissolved in hydrochloric acid, and more especially the resultant chlorosuccinic acid. This substance crystallises in short lustrous prisms, it melts at about 174° with decomposition, and is lævorotatory, $[\alpha]_D = -19{\cdot}67^\circ$, at the temperature of the air. The silver and copper salts may be obtained as precipitates nearly insoluble in water. The acid agrees closely in melting-point with the dextrorotatory chlorosuccinic acid obtained from malic acid by Walden, and the values for the specific rotatory power of the two compounds are nearly the same. Walden's acid showed a specific rotatory power of 20·6° to 20·8°. The lower value for the lævorotatory acid is probably due to its partial dissociation into hydrogen chloride and fumaric acid when dissolved in water.

*47. "*A Property of the Non-luminous Atmospheric Coal-gas Flame.*" By **Lewis T. Wright**.

The author points out that the separation of the atmospheric gas flame (Bunsen flame) into two distinct parts described by Teclu (*J. Pr. Chem.*, xliv., 246) and Smithells and Ingle (*Trans.*, lxi., 204), was discussed by himself in June, 1887, in a paper "On the Induction of the Explosive Wave and an Altered Gaseous Condition in an Explosive Gaseous Mixture by a Vibratory Movement," an abstract of which was published in *Roy. Soc. Proc.*, xlii.

The experiments described in that paper were made with a mixture of coal-gas and air in combustion tubing of $\frac{3}{8}$ in. diameter.

The analytical results of that enquiry confirm those obtained by Smithells and Ingle, and bring out a characteristic of the inner flame. It is able to maintain a stationary position in the glass tube against various velocities of egress of the gaseous mixture. The distribution of the oxygen amongst the three principal products of combustion, viz., carbon monoxide, carbon dioxide, and water, differs, however, with the velocity of the gaseous current in the tube. The carbon dioxide increases, and the carbon monoxide decreases with increased velocity of the gaseous current.

*48. "*Diortho-substituted Benzoic Acids. I. Substituted Benzoyl Chlorides.*" By **J. J. Sudborough**, Ph.D.

In this paper, the author, after referring to the work of V. Meyer and Sudborough on the esterification of aromatic acids—in which it is shown that diortho-substituted benzoic acids as a rule yield no esters, when their alcoholic solutions are saturated with dry hydrogen chloride—describes the preparation and properties of the following substituted benzoyl chlorides. *o*-, *m*-, and *p*-Brombenzoyl chloride; 2·4, 3·5, and 2·6 dibrombenzoyl chloride; 3·4·5 and 2·4·6-tribrombenzoyl chloride; 2·3·4·6-tetrabrombenzoyl chloride; 2·6-dinitrobenzoyl chloride; 2·4·6-trinitrobenzoyl chloride; together with the acid amides and esters obtained from them.

In each case, experiments were made by boiling 0·5 grm. of the acid chloride with 20 c.c. of an 8 per cent solution of pure sodium hydrate. These experiments have shown—

1. That the acid chlorides which do not contain bromine atoms in the ortho-positions are readily decomposed, in most cases, before the solution begins to boil, in the others within ten seconds of boiling.
2. That those acid chlorides which are substituted by one bromine atom in an ortho-position are somewhat more stable, and are only completely decomposed after boiling for two to three minutes with the alkaline solution.

3. That acid chlorides with bromine atoms in the two ortho-positions are extremely stable.

Thus, while the 2 · 6-dibrombenzoyl chloride is entirely decomposed after boiling for thirty-five minutes with the alkaline solution, only 28—30 per cent of the 2 · 4 · 6-tribrom chloride is decomposed after boiling for one hour. and of the tetrabrom chloride from 6 to 8 per cent is decomposed after boiling for the same length of time with the caustic soda solution.

The decomposition of the di- and tri-nitrobenzoyl chlorides could not be quantitatively followed, as other reactions occur at the same time, and a deep red solution is formed in both cases.

The author intends investigating the corresponding methyl- and chlorbenzoyl chlorides in order to see whether the same rules hold for these as for the brom-derivatives.

*49. "*Diortho-substituted Benzoic Acids. II. Hydrolysis of Aromatic Nitriles and Acid Amides.*" By J. J. Sudborough, Ph.D.

For the preparation of large quantities of substituted benzoic acids from the corresponding nitriles, the author recommends a modified form of the method suggested by Bouveault (*Bull. Soc. Chim.*, [3], 9, 368). Whereas Bouveault states that the method is only applicable to those nitriles which are converted into the acid amides by heating with 90 per cent sulphuric acid for several hours on the water-bath; the author of this paper shows that the method can be used for other nitriles, provided the sulphuric acid mixture is heated on the sand-bath to 120—130° for an hour or so. The acid amides thus obtained are converted into the corresponding acids by means of sodium nitrite according to Bouveault's method. The yields are extremely good and it would seem that the method is of very general application. The following acids have been obtained by the method :—

p-Brombenzoic acid, 2 · 4, and 2 · 6-dibrombenzoic acid, 2 · 4 · 6-trichlorbenzoic acid.

The 2 · 6-dibrombenzoic acid is readily soluble in water and separates out on standing in the form of long needles or short prisms of m. p. 146·5°.

The 2 · 4, and 2 · 6-dibrombenzamides, which were obtained as intermediate products in the preparation of the corresponding acids, differ most remarkably in their properties. Thus, whilst the 2 · 4-compound is completely converted into the corresponding acid by heating to 170—180° in a sealed tube with 80 per cent sulphuric acid, the 2 · 6-amide under the same conditions is entirely unacted upon.

This behaviour of the two amides is quite analogous to that of the corresponding acid chlorides towards alkalis (see preceding abstract). A study of the work of Claus and his pupils (*J. Pr. Chem.*, [2], xxxvii., 197; *Annalen*, cclxv., cclxvi., cclxix., cclxxiv.) on the hydrolysis of various substituted aromatic nitriles, shows that the diortho-substituted benzamides are, as a rule, remarkably stable towards hydrolysing agents. Thus, while substituted benzonitriles are converted into the corresponding acids by boiling for some time with fairly concentrated sulphuric acid, those nitriles which are substituted in the two ortho-positions yield the acid amides and not the acids under the same treatment. An important exception to this rule appears to be the 2 · 6-dichlorbenzamide, as Claus and Weil state that the 2 · 6-dichlorbenzonitrile is directly converted into the acid when heated with sulphuric acid in sealed tubes at 150°. This appears remarkable when compared with the behaviour of the corresponding brom-compounds, and the author hopes to investigate the hydrolysis of various substituted benzamides.

*50. "*Note on the Action of Sodium Ethylate on Deoxybenzoïn.*" By J. J. Sudborough, Ph.D.

In attempting to prepare substitution-derivatives of deoxybenzoïn, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}C_6H_5$, by heating together deoxybenzoïn, sodium ethylate, and various halogen compounds in sealed tubes at 150—160°, the author always observed the production of a considerable quantity of stilbene (diphenylethylene). Experiments have shown that this is produced by the action of sodium ethylate on deoxybenzoïn at 160°, and that a substance which is very soluble in alcohol, and has a much lower m.p., is formed at the same time. On analysis this latter compound proved to be hydroxydibenzyl, $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}C_6H_5$. It is evidently produced from the deoxybenzoïn by the reducing action of the sodium ethylate. This compound, when heated, loses water, and is converted into stilbene. The hydroxydibenzyl, when re-crystallised from hot ligroin (b.p. 40—50°), forms long, silky needles which melt at 63°.

When deoxybenzoïn is heated with sodium methylate no trace of stilbene is formed. This is interesting when compared with the results obtained by Lobry de Bruyn on the action of sodium ethylate and methylate on various aromatic nitro-compounds.

De Bruyn shows that whilst the methylate acts as a substituting agent, replacing a nitro- by a methoxy-group, the ethylate at the same time acts as a reducing agent, producing more or less of the corresponding azo-compounds.

51. "*A Constituent of Persian Berries.*" By A. G. Perkin and J. Geldard.

Persian berries, as is well known, contain a glucoside xanthorhamnin (α-rhamnegin) decomposable by acids into isodulate and a colouring-matter rhamnetin. With hydriodic acid rhamnetin yields methyl iodide and quercetin, the colouring-matter of quercitron bark (Herzig, *Monatsch.*, ix., 548—561). It is consequently a quercetin monomethylether, $C_{16}H_{12}O_7$. According to earlier workers there is also present a second glucoside which gives a colouring-matter more soluble in alcohol than rhamnetin, and therefore called β-rhamnetin. Herzig (*Monatsch.*, x., 561—567), when studying this subject, isolated from the berries a glucoside which he regarded as a loose double compound of xanthorhamnin and a glucoside of quercetin (quercitrin ?), for by decomposition it gave a mixture of rhamnetin and quercetin. Hence β-rhamnetin appeared to be quercetin.

In this paper it is shown that Persian berries contain a third substance readily isolated from the mixed colouring-matters by extraction with toluene. It forms long yellow needles somewhat resembling anthraquinone, melting at 214—215° (quercetin and rhamnetin both melt above 280°), has the formula $C_{17}H_{14}O_7$, and crystallises from acetic acid with 2 mols. of acetic acid of crystallisation. The triacetyl compound $C_{17}H_{11}O_7\,(C_2H_3O)_3$, colourless needles, melts at 154—155°; the tribenzoyl compound $C_{17}H_{11}O_7(C_7H_5O)_3$, colourless needles, melts at 204—205°; and the dibromo-compound $C_{17}H_{12}O_7Br_2$, yellow needles, decomposes at 250° before melting. By the action of hydriodic acid it yields quercetin and 2 mols. of methyl iodide, and is therefore a *quercetin dimethyl ether*. Rhamnazin, as we have called this substance, is nearly devoid of dyeing properties. Quercetin being a colouring-matter, contains at least two hydroxyls in the ortho position to one another, and in rhamnazin therefore one or two of these hydroxyls must be replaced by a methoxy group, causing this loss of colouring power.

It is known that an aqueous extract of Persian berries ferments at 30—40°, depositing a yellow powder, the supernatant liquid being of an orange-brown colour. This powder is here shown to be a mixture of rhamnetin and rhamnazin with but a trace of quercetin. The supernatant liquid when boiled with acids gives a considerable quantity of quercetin only. It appears therefore that the ferment contained in the berries (Ward and Dunlop, *Annals of Botany*, 1889), while readily decomposing xanthorhamnin and the glucoside of rhamnazin at this temperature, exerts but little influence upon the glucoside of quercetin also present.

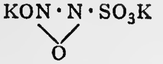
The colouring-matters of Persian berries are rhamnazin quercetin dimethyl ether), rhamnetin (quercetin mono-(methyl ether), and quercetin, $C_{15}H_{10}O_7$, itself.

52. "*Potassium Nitrososulphate.*" By E. **Divers**, F.R.S., and T. **Haga**.

According to Raschig, there are two salts of the composition of Pelouze's potassium nitro(so)sulphate, prepared almost in the same way from nitric oxide and potassium sulphite. Hantzsch has recently (*Ber.*, xxvii., 3264) investigated this matter in connection with his studies of the stereoisomerism of nitrogen compounds, and finds that he cannot get the salt like Pelouze's salt, which Raschig got, but only one which is identical with Raschig's other, or second, salt. There are therefore, it would seem, two isomeric salts, one being Pelouze's salt and the other Hantzsch's. Raschig alone got both these salts.

The authors are convinced that no isomer of Pelouze's salt has been shown to exist. In the first place, Raschig and Hantzsch have confounded the former's first salt with Pelouze's, through supposing that the latter salt is precipitable by dilute solutions of barium salts. In the second place, this first salt prepared by Raschig appears, from his description, to have been so particularly like another obscurely known salt obtained by him, and called "basic potassium dihydroxylaminesulphonate," as to be at present almost indistinguishable from it (as described), whether in composition, in chemical properties, or even in preparation, if only, as might have happened, some nitric peroxide or air got into the sulphite solution along with the nitric oxide. In the third place, a re-examination of Pelouze's salt, in the light of Hantzsch's observations, shows that no sufficient grounds exist for asserting the non-identity of Hantzsch's salt, or the second salt of Raschig's, with Pelouze's salt.

The authors point out that nitrososulphates do not show such near analogy to isonitramines as Traube believes them to do, and regard them as displaying the constitution of a sulphate, $KON_2{\cdot}O{\cdot}SO_3K$, rather than that of a sulphonate,—



$$\underbrace{KON\cdot N}_{O}\cdot SO_3K$$

(Hantsch).

Potassium nitrososulphate behaves like a sulphonate in giving a barium-potassium salt (and so also does potassium ethyl sulphate, though a true sulphate), but it also gives barium sulphate instantaneously when acidified, and no sulphonate does that.

53. "*The Milk of the Gamoose.*" (Second notice). By H. **Droop Richmond**.

In a previous paper (*Trans.* lvii., 758) the author described a sugar existing in the milk of the gamoose, differing in its properties from milk sugar. He now finds that this sugar is not always present in the milk of these animals, and describes experiments showing the difference between milk examined in January, 1890, and August, 1891.

PHYSICAL SOCIETY.

Ordinary Meeting, May 10th, 1895.

Captain W. de W. **Abney**, President, in the Chair.

Mr. **Herroun** read a paper "*On the Iodine Voltameter.*"

After referring to the usual methods of determining the value of the small currents used in calibrating galvanometers and other apparatus for measuring small currents, and discussing the errors to which they are subject, the author gave his reasons for selecting iodine. He did this since, with the exception of mercury in the mercurous state, iodine has the largest electro-chemical equivalent, and, in addition, by titration with sodium thiosulphate, it is possible to determine the quantity of iodine liberated with a greater accuracy than can be obtained by weighing a deposit of copper or silver with the balance. The solution employed in the voltameter contains 10 to 15 per cent of zinc iodide. If care is taken to leave a small piece of metallic zinc in this solution, no free iodine is liberated on keeping, unless the solution is exposed to a strong light for some time. The anode consists of a plate of platinum at the bottom of a tall and fairly narrow beaker. The wire leading the current to the anode is encased in a glass tube, so that the iodine is only liberated at the bottom of the beaker, where, on account of its great density, it tends to collect. The kathode consists of an amalgamated zinc rod, which, to prevent loose particles of zinc falling down into the iodine, is surrounded by a piece of filter-paper or vegetable parchment. In an electrolysis lasting for as long as two hours none of the iodine is found to diffuse up to the part of the solution near the zinc kathode. Where, on account of the extreme feebleness of the currents employed, it is necessary to allow the electrolysis to continue for longer than two hours, a U-tube is used with two small plugs of asbestos at the bend, the anode being in one limb and the kathode in the other. With this form of voltameter, even after the current has flowed for several days, no signs of iodine have been found in the limb containing the kathode. On account of the production of electric convection currents, the iodine voltameter does not seem to be quite so suitable for the accurate measurement of strong currents.

After the current is stopped the zinc electrode is immediately removed, the solution stirred, and the amount of iodine liberated determined by titration with sodium thiosulphate. The author finds that a convenient strength of the thiosulphate solution is one in which 1 c.c. corresponds to the amount of iodine liberated by 5 coulombs of electricity. This solution contains 12·8375 grms. of pure crystallised sodium thiosulphate per litre. It is possible to perform the titration to within 0·1 c.c., which corresponds to 0·5 coulomb, or if the electrolysis lasted one hour to $\frac{1}{7200}$ ampère. In a comparison made with a silver voltameter, the current as deduced from the silver was 0·0264 ampère, and that deduced from the iodine 0·0266. The author considers that part of the difference may be due to the effect of oxygen dissolved in the silver nitrate.

Prof. **Carey Foster** considered this process for measuring currents a most valuable one. The idea of using a volumetric method for measuring currents was, to him, new. He did not, however, see the advantage of using a substance with a high electro-chemical equivalent if a volumetric method was employed to estimate the quantity of the substance liberated. It would be possible to use a chloride, though in this case the titration would probably be less accurate.

Prof. **Silvanus Thompson** said he thought the method would be very valuable, but he would like to know if any error was likely to arise if too great a current density was employed. The number the author had assumed for the atomic weight of silver (108) was only approximate; if the more accurate value 107·7 were used the agreement between the results obtained with the silver and iodine voltameters would be improved.

Mr. **Trotter** asked what was the largest current that could be accurately measured.

Mr. **Enright** said he had used porous diaphragms in iodine voltameters, and found that the iodine collected in the positive compartment, while the water was driven over into the negative compartment. With strong currents it was possible to get almost pure iodine left in the one compartment.

Mr. **Watson** thought that since the value for the electro-chemical equivalent of iodine used by the author was deduced from Rayleigh's value of the electro-chemical equivalent of silver, and that Rayleigh's experiments were performed in air, the difference obtained with the silver and iodine voltameters could hardly be due to the cause suggested.

Mr. **Elder** warned the members that volumetric measurements were not so accurate or easy as they seemed. He particularly mistrusted a solution of sodium thiosulphate, since he had found a solution of this substance to change even in twenty-four hours. The difficulty of accurately reading the burette might be overcome by weighing the burette and its contents before and after the titration.

The author, in his reply, said that with the size of electrodes he used (about 9 sq. c.m. surface), 0·1 ampère was the maximum current it was safe to use. The only substance likely to be produced by too great a current density was periodate, which, since it was insoluble, would immediately be noticed. The influence of the dissolved oxygen was only appreciable with small currents where the electrolysis lasts some time; while in Rayleigh's experiments large currents were employed.

The Chairman, while returning thanks to the author for the paper, mentioned that in his experience he had found zinc salts to be very untrustworthy.

Mr. A. Sharp read a paper entitled "*A New Method in Harmonic Analysis.*"

The author in this paper applies the principle of the form of harmonic analyser for giving direct readings of the amplitude and epoch of the various constituent harmonic terms previously described by him, to the performance of harmonic analysis without the use of an instrument. The kinematic principle is as follows:—Let the curve to be analysed be drawn, with a scale of abscissæ such that the period is 2π. Let a wheel, w, roll on the paper and be connected with a tracing-point, P, in such a manner that as P moves uniformly in the x direction the axis of the wheel w turns uniformly counter clockwise in a horizontal plane, and the distance rolled through during any short interval is equal to the corresponding displacement in the tracer P in the y direction. The curve traced out by w the author calls the roller curve, and from the vector joining the initial and final points of this curve the amplitude and epoch can be determined. Suppose the periodic curve consists of a portion of the curve,

$$y = a_0 + a_1x + a_2x^2 + a_mx^m,$$

repeated over and over again; then if the tracer is taken round this periodic curve you get a rolled curve, which may be called the first rolled curve. If now the curve whose ordinates are—

$$\frac{dy}{dx}$$

is traced out, the roller curve obtained is the evolute of the first, and so on for—

$$\frac{d^2y}{dx^2}, \text{\&c.}$$

The author gives two worked examples, and compares the values of the coefficients obtained with those given by the harmonic analyser of the Guild's Central Technical College.

Prof. Henrici said he had not received the paper in time to thoroughly master it, but he thought that, at any rate for curves where no discontinuity occurred, the relation found by the author between the roller curves was always true, the last evolute being a point, and the one before that a circle. The interesting point was whether the method was capable of being used for practical purposes, for it occupied a place with respect to harmonic analysis similar to that occupied by Simpson's rule in planimetry.

Prof. Silvanus Thompson asked if the author had devised a form of mechanism capable of fulfilling the kinematical conditions given at the commencement of the paper.

The author, in his reply, said he had devised such a mechanism, and that it was described in his previous paper. In addition he had since invented a more practicable form, which he had patented.

The Chairman said the Society ought to congratulate itself on the large number of important papers dealing with harmonic analysis and planimetry that had lately been communicated.

NOTICES OF BOOKS.

Principles and Practice of Agricultural Analysis. A Manual for the Estimation of Soils, Fertilisers, and Agricultural Products. For the Use of Analysts, Teachers, and Students of Agricultural Chemisty. Vol. I.—Soils. By Harvey W. Wiley, Chemist to the U. S. Department of Agriculture. 8vo., pp. 607. Easton: Chemical Publishing Co. 1894.

In examining this elaborate work we may first give a glance at the author's nomenclature. He adopts a certain half-way reform in chemical terminology. Thus he deletes the final *e* in the names of the halogens and their compounds, as well as "oxid" and "sulphid." He writes "sulphur" with *f* instead of the traditional *ph.* But we may ask why, having gone so far, he does not take an additional step, which would not be in the least confusing to the reader? Why not, in the names of the halogens, simply eliminate the appendage "ine," and write fluor, chlor, brom, and iod? Why does he not cut off the needless "us" from phosphorus, and call this element simply *phosphor?* By so doing he would have given his support to a desirable improvement in the language of inorganic chemistry.

Turning from manner to matter, we must congratulate Mr. Wiley on the judicious thoroughness of his compilation. The volume before us, devoted to the consideration of soils, consists of eight parts, treating respectively of the origin of soils, of sampling for analysis, of the physical properties of soils, of mechanical—or, as it might perhaps be better called, physical—analysis, of the estimation of gases in soils, of the chemical analysis of soils, of the determination of nitrogen in its various states, and of the special examination of waters. Each of these parts concludes with a special bibliography. The remarks on the origin of soils suggest important questions connected with the genesis of organisms, but into these—as having no bearings on agricultural practice—the author does not enter. We may ask whether he does not go too far in regarding boron as a true plant-food, and whether he is not chargeable with a sin of omission in failing to condemn the use of boric acid as a food preservative? Manganese and copper have at last as good a claim to rank as plant-foods as has boron.

The importance of a microscopic examination of soils and rocks accompanying the chemical analysis is justly insisted on. The different agencies, vital and lifeless, which effect the disintegration and to some extent the decomposition of rocks, are discussed to some extent. The author holds that the power of ice in effecting "rock decay" has been somewhat over-rated, and that the entire absence of frost promotes the process. In discussing the evils of soils loaded with alkalies—one of the greatest enemies which the subtropical agriculturist has to encounter—he points out that irrigation without drainage intensifies the mischief. Peaty soils appear to bear in America the unpleasing name of "mucks."

The instructions for sampling soils are very useful. We have known analysts occur most unmerited blame for their reports on specimens unfairly taken.

In Part 3 we do not see it mentioned that the black colour of a soil may be due to sulphur compounds acting upon iron oxides.

The instructions for physical analysis are highly valuable, and bring into prominence not a few considerations which should not be neglected if analysts were allowed time to do justice to the specimens upon which they operate. Staining particles of silt for microscopical examination, as is done in case of bacteria, may often throw an instructive light upon the capabilities of a soil.

The 6th and 7th Parts, giving instructions for the chemical analysis of soils, and especially for the determination of their combined nitrogen, are very elaborate. Concerning manganese we find the admission that this element "exists in all plants, and its presence in small quantities seems necessary to vegetation." The method recommended for its determination is that of Leclerc. It is recognised that in some cases "the introduction of iron as a fertilising element may be useful."

Sodium chloride is—rightly according to our experience—regarded as injurious in the proportion of 1 lb. to 1000 lbs. of earth.

Concerning the supply of nitrogen to plants, the author does not recognise its absorption from the air without the co-operation of micro-organisms.

In Part 8, describing the analysis of agricultural waters, we find no mention of the method of Frankland. Its rival process is solely ascribed to Nessler. This chemist certainly discovered the reaction which here comes into play, but it is generally understood to have been rendered quantitative by Wanklyn, a fact never, we believe, denied in the long and bitter controversy on the merits of the two processes.

A few expressions to be encountered in this work will scarcely be understood on this side of the Atlantic. What, for instance, is a "truck farm"?

We hope that the second volume will prove equal in value to the one before us.

Organic Chemistry, Theoretical and Practical, adapted to the Requirements of the Science and Art Department, and of the London University. By ISAAC SYDNEY SCARF, F.I.C., F.C.S., Professor of Chemistry and Experimental Physics in the City of London College, and a Science Master in the City of London School. With 36 Illustrations and 180 Experiments. Post 8vo. London and Glasgow: W. Collins, Sons, and Co., Limited.

IT may perhaps be some faint consolation to the Chinese, amidst their reverses, to learn that the system of education which has helped so powerfully to keep them in a state of non-age, is still obstinately adhered to by a nation which proclaims itself the great incarnation of progress. No work ever published, in China or in Britain, could be more openly and avowedly examinational than the one before us. In its very title it is described as being "adapted to the Requirements of the Science and Art Departments, and of the London University." We must beg permission to express a conviction that the requirements of a Science and Art Department or of any true University should, on the contrary, be adapted to the state of Science!

In the Preface, brief as it is, we find further reference to the same subject. The book is said to be "written primarily for students preparing for the elementary examinations of the Science and Art Department." In the next sentence we are told that it contains "sufficient experimental matter to make it available as the laboratory companion of candidates for the Int. N.B. and final B.Sc. of the London University and other examinations." Lastly comes the further information that "certain portions of the work may be omitted by those who wish to qualify for a pass only in theoretical and practical organic chemistry." *Eheu!*

On the other hand, we are glad to perceive that the author is evidently not satisfied with the termination *ine* for the names of the alkaloids; at least he gives the form in *ia* as a synonym. We wish the example could be generally followed. The recent Inland Revenue ukase, by which methylated spirt is for most purposes spoiled by the addition of mineral naphtha, is mentioned without a word of protest. We have often wondered who devised this unhappy expedient.

Many readers will be surprised at the statement that gin is obtained from potatoes. Unless some recent change has been made this popular spirit, both in Holland and England, is obtained from grain, in company with juniper berries. A very vile whisky, rich in fusel, is distilled from potatoes in north-eastern Germany. It is an edifying sight to see a Pomeranian peasant take a glass of this spirit, and fling it down his throat with a shudder.

Caffeine and theobromine are merely mentioned in passing.

A striking feature of the work is an Appendix of ten pages, consisting of questions taken ftom the examination papers of the Science and Art Department, and of the University of London

Our opinion is that the author could produce a more valuable work had he not the fear of the Department ever before his eyes.

The Extra Pharmacopœia. By WILLIAM MARTINDALE, F.C.S., late Teacher of Pharmacy and Demonstrator of Materia Medica at University College.
Medical References and a Therapeutic Index of Diseases and Symptoms. By W. WYNN WESTCOTT, M.B. Eighth Edition. London: H. K. Lewis. 1895.

THE fact that this manual has now reached its eighth edition is sufficient proof that it is duly appreciated by the medical profession and by the pharmacists.

In addition to many minor novelties, we must particularly notice a section on antitoxins, serums, and lymphs. These substances are alternated morbid products, which in some cases, if injected into the tissues of a man or other animal, exert a curative or even an immunifying effect. Of these agents, excepting vaccine, the oldest and best known is Pasteur's antitoxin for rabies. The death-rate among persons bitten, without this treatment was about two hundred per thousand, whilst by means of Pasteur's treatment it is reduced to from two to three per thousand. The treatment for tetanus, devised by Cattani and Tizzoni, is still *sub judice.* If thoroughly established it will be of immense value to the army in India, where wounds, even if trifling, are often followed by fatal tetanus.

The balance of results seems unfavourable as regards Koch's tuberculin. The antitoxin for diphtheria appears to have been more successful. We must not forget that all remedial agents of this type are strenuously denounced by the "Anti-vaccinationists." They have vehemently opposed the formation of the British Institute of Preventive Medicine.

It is painfully interesting to notice how the use of arsenical cosmetics—the so-called Styrian vice—is spreading in Britain. We do not, of course, find any such preparations recommended in the work before us, but they are being increasingly advertised, and of some of them it is said that they are inventions of doctors.

CORRESPONDENCE.

THE ATOMIC WEIGHT OF YTTRIUM.

To the Editor of the Chemical News.

SIR,—I read with interest Mr. Jones's paper on the atomic weight of yttrium (CHEMICAL NEWS, lxxi., p. 170). That paper suggests to me a few remarks, which I beg leave to submit to the reader. The bearing of the chemistry of the rare earths on the periodic law gives to their metals an importance which they otherwise would not be entitled to.

It is necessary for my purpose to complete the history of the determination of the atomic weight of yttrium. Mr. Jones does not seem to be acquainted with the following facts:—

In February, 1866, I published four determinations of the atomic weight of yttrium, giving an average of 87·7.

M. Berlin, of Stockholm, found from 87 to 87·3 for the same metal.

In his "Elements of Chemistry" M. Mendeleeff says that he found 87·9 in 1871.

My yttria and that used by Mr. Berlin were white.

Prof. Clève's results, published later, are somewhat higher (89·7), but his yttria was pale yellow.

Moreover, the history of the question shows that the nearer to purity the paler yttria is, and the lower its molecular weight. From an yttria corresponding to 89·7 I readily separated a more coloured earth. Berzelius, Scherer, Mosander, Marignac, and Crookes, all agree that yttria is white.

Although evidently inaccurate, Prof. Clève's results are adopted by all chemists, probably on account of the reputation of the Upsala *savant* and in order to meet the requirements of the periodic law.

Now I come to the point. Working on a scandia free yttrium oxide, I find my results of 1866 correct. Thus Mr. Jones, M. Berlin, and myself, experimenting on white yttria, have obtained results the divergence of which can hardly be accounted for on the ground of experimental errors :—

Jones	89
Delafontaine ..	87·7 (87·3 now)
Berlin	87·3.

We are then led to suppose that yttria without any admixture of scandia is not a homogeneous compound. This is what I am trying to find out, and why I do not publish now my recent numerical results. As is well known, Mr. Crookes discovered, several years ago, a number of facts raising the same question.

The fact that the periodic law requires Y = 89, instead of any lower figure, has not in my mind as much weight as with other chemists. Having worked, and being still working, on large quantities of materials extracted from samarskite, fergusonite, euxenite, polycrase, and gadolinite, I have come to the conclusion that the atomic weight of scandium is lower than 44. If the periodic law absolutely requires 44, then scandium is not ekaboron. Philippium, denied by some eminent chemists, is nevertheless well characterised chemically, and its spectrum contains lines not belonging to yttrium and terbium.

Chemists with a sufficient supply of raw material will find that the old didymium oxide is a mixture of at least four compounds—praseo-didymium, neodidymium, samarium oxide, and another forming dichroic purplish salts.

Gadolinium is identical with decipium, and disappears from the list.—I am, &c.,

P. Delafontaine.

South Division High School,
Chicago, April 27, 1895.

ATOMIC WEIGHTS.

To the Editor of the Chemical News.

Sir,—Although it might be urged that until we know more about helium and argon, and the elemental gases probably associated with them, it would be well to cease speculation concerning the Periodic Law, I do not think that any harm can be done by pointing out certain interesting relationships between the magnitudes of the atomic weights of the elements.

I therefore venture to call attention to an arrangement of the elements, according to their atomic weights and valencies, which not only indicates that there are probably some missing elements, but also enables their atomic weights to be roughly calculated.

In the first column of the accompanying Table the elements having odd valencies are entered in the order of their atomic weights. Between Nb and Rh space is left for an element predicted by Mendeleeff. Against them in col. 2 are given their atomic weights, and in col. 3 the differences between consecutive atomic weights.

Atomic Weights of Elements.

Perissads.					Artiads.	
Element. 1.	At. wt. 2.	Differences. 3.	 4.	 5.	At. wt. 6.	Element. 7.
H	1·00				0·00	—
		6·02	−1·02	5·00		
Li	7·02				5·00	?
		3·98	+0·12	4·10		
B	11·00				9·10	Be
		3·03	−0·13	2·90		
N	14·03				12·00	C
		4·97	−0·97	4·00		
F	19·00				16·00	O
		4·04	−0·04	4·00		
Na	23·04				20·00	?
		3·97	+0·33	4·30		
Al	27·01				24·30	Mg
		4·02	+0·01	4·03		
P	31·03				28·33	Si
		4·43	−0·70	3·73		
Cl	35·46				32·06	S
		3·68	+0·26	3·94		
K	39·14				36·00	?
		4·96	−0·88	4·08		
Sc	44·10				40·08	Ca
		7·30	+0·75	8·05		
V	51·40				48·13	Ti
		3·60	+0·57	4·17		
Mn	55·00				52·30	Cr
		3·70	+0·02	3·72		
Ni	58·70				56·02	Fe
		4·70	−1·36	3·34		
Cu	63·40				59·36	Co
		6·50	−0·56	5·94		
Ga	69·90				65·30	Zn
		5·19	+1·81	7·00		
As	75·09				72·30	Ge
		4·86	+1·94	6·70		
Br	79·95				79·00	Se
		5·55	−1·55	4·00		
Rb	85·50				83·00	?
		3·50	+1·00	4·50		
Y	89·00				87·50	Sr
		5·00	−2·50	2·50		
Nb	94·00				90·00	Zr
		4·50	+1·20	5·70		
?	98·50				95·70	Mo
		4·50	+1·45	5·95		
Rh	103·00				101·65	Ru
		4·93	−0·23	4·70		
Ag	107·93				106·35	Pd
		5·77	−0·02	5·75		
In	113·70				112·10	Cd
		6·60	+0·40	7·00		
Sb	120·30				119·10	Sn
		6·55	−0·65	5·90		
I	126·85				125·00	Te

In col. 7 are entered the elements having even valencies. Be is not entered on a line with H, but on a line with B, which it immediately precedes on the atomic scale. Similarly C is on a line with N, which it also immediately precedes. And so on with the other elements having even valencies. In col. 6 are entered their atomic weights, and in col. 5 the differences between consecutive atomic weights.

Omitting the first line the vacant spaces are regarded as indications that elements may be found to fill them. Such elements fall between H and Li, F and Na, Cl and K, Br and Rb, and so on with increasing atomic weight. Their atomic weights are roughly 5, 20, 36, 83, &c.

In col. 4 are given the differences between cols. 3 and 5. The agreement, it will be seen, is fairly good, large and small values in cols. 3 and 5 alternating in unison.

Any additional elements put in, even if they did not produce greater discrepancies than col. 4 now shows, would interfere with the regular increase and decrease in valency.

Elements of greater atomic weight than iodine have not been put in the table, as their atomic weights are in some cases uncertain, and the figures throw no additional light upon the subject.—I am, &c.,

R. M. Deeley.

10, Charnwood St., Derby.

ACTION OF HYDROGEN GAS ON AMORPHOUS PHOSPHORUS.

To the Editor of the Chemical News.

Sir,—It would interest me, and probably others, to know if any of your readers have repeated an experiment recently described in the Chemical News, namely, the direct combination of hydrogen with amorphous phosphorus to form phosphine.

My attempts have not proved successful. In the first experiment some amorphous phosphorus was heated in a tube through which hydrogen was passing, and the gas, after traversing a wash-bottle containing water, was led to a pneumatic trough. A gas escaped which fumed in the air, but did not spontaneously inflame, the fuming appearing to be due to the presence of finely-divided phosphorus carried over mechanically.

In the second experiment a piece of combustion-tube was bent at right angles, and some amorphous phosphorus was placed in the horizontal part of the tube, whilst the vertical limb dipped into mercury. Hydrogen was passed over the phosphorus, which was heated until about half of it had been transformed into the ordinary modification; the gas was then passed until the tube cooled, and the hydrogen apparatus was sealed off. On heating the amorphous phosphorus in the hydrogen no diminution of volume was observed.

In the third experiment dried hydrogen was passed over amorphous phosphorus which had been washed with water until neutral and then dried. The phosphorus was first gently heated, just sufficiently to change it to the ordinary variety, and later the tube was raised to a higher temperature. The resulting gas was passed through a wash-bottle containing water, and then through a U-tube filled with wet glass beads to remove suspended phosphorus, and finally into a solution of cupric sulphate; but no precipitate of phosphide of copper resulted.

It is probable that I have not worked under exactly the proper conditions, and I should be obliged to any one who has been more fortunate than myself if he will give me the benefit of his experience.—I am, &c.,

Herbert McLeod.

Cooper's Hill, Staines,
May 13, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 17, April 29, 1895.

New Researchss on the Combining Heats of Mercury with Elements. — Raoul Varet.—This thermochemical memoir does not admit of useful abstraction.

Researches on Manganese.—Charles Lepierre.—The author, continuing the study of the action of fused ammonium sulphate, or better bisulphate, upon metallic salts, shows the results obtained with manganese. On adding to ammonium sulphate about one-fifth of its weight of crystalline manganese sulphate there is obtained, after the expulsion of the water of crystallisation (180°—200°), a deposit of large crystals of the cubic system, which after decanting off the excess of the ammoniacal salt and purification with boiling alcohol at 70 per cent, corresponds to the formula $2SO_4MnSO_4.Am_2SO_4Mn$. On heating this anhydrous salt either alone or in the liquid in which it has been formed it is converted at 350° into anhydrous manganous salt. This salt is very hygroscopic; sp. gr. at 12° is 3·14. Hence manganese behaves like nickel and cobalt and does not, like iron, form super-oxygenated salts. The author has obtained an alum, anhydrous ammonium manganic $(SO_4)3Mn_2.SO_4Am_2$.

Campholenic Amides and Acids.—A. Béhal.—The author has examined the three amides fusible respectively at 86°, 130·5°, and 106°. He concludes that the amide fusible at 106° is a molecular compound of the amides fusible at 86° and 130·5°.

Double Compounds of Anhydrous Aluminium Chloride with Nitro-compounds of the Aromatic Series.—G. Perrier.—The author, referring to the researches of Stockhausen and Gattermann, states that he has found that most of the compounds belonging to the various functions of organic chemistry combine with aluminium chloride. Among those experimented on are nitrobenzene, paranitrotoluene, nitronaphthaleine-α, dinitrobenzene (meta and 1.2.3), and paranitranisol.

On an Error which may Occur by the Use of Fehling's Liquid in the Detection of Sugar in the Urine of Persons under Treatment with Sulphonal.—Ph. Lafon.—Fehling's solution in such cases may give a strong yellow precipitate, though the same urine if examined with the polari-saccharimeter under yellow monochromatic light gives no dextro-deflection, the characteristic of diabetic sugar, but a faint deflection to the left.

Panification of Brown Bread.—James Chappuis.—This is the opening of a "*pli cacheté.*" The bread in question is the result of the action of a diastase, cerealine, of Megé Mouriès upon the paste. The diastase of wheat (and probably of other grain) is destroyed by oxygenated water. It is possible to make white bread with flour of all qualities.

Causes which Produce the Colour of Brown Bread.—Léon Boutroux.—Gluten can give colour to bread on desiccation but not on fermentation. Bran may give colour to bread by the action of atmospheric oxygen in presence of water, but not by fermentation. The acidity of yeast, far from being to be feared in this respect, is a protection against browning.

Zeitschrift für Anorganische Chemie,
Vol. vii., Part 6.

Transformation of Black Mercury Sulphide into the Red Form, and on the Density and Specific Heat of both Substances.—W. Spring.—The elasticity of solids is only perfect in cases where the presence of allotropic modifications is excluded. Otherwise the substance assumes a denser state, corresponding to the decrease of volume to which they have been subjected. It appears that for solids as well as for gases there is a critical point, above or beneath which an increased pressure occasions no change in the condition of the substance. The black modification of mercury sulphide must undergo a decrease of volume in order to pass into the red state. This explains a number of observations made upon mercury sulphide. If the black sulphide is vigorously rubbed in an agate mortar we see a red streak where the pestle has acted. A temperature of 410° is the critical-point above which the red modification cannot exist.

Preservation of Chemically Pure Alkaline Solutions.—Alexander von Kalecsinsky.—The author fits into a straight-sided flask a beaker of sheet silver or platinum, so that a small place is left at the sides and the bottom between the metal and the glass. A silver or platinum tube passes through the stopper to near the bottom. A glass tube also passes through the stopper but does not dip into the liquid. On blowing into this latter tube the alkaline liquid ascends out of the metal pipe, and can be allowed to escape for use.

Some Methods for Separating Phosphoric Acid as an Alkaline Phosphate from the Calcium and Ferric Phosphates.—E. A. Schneider.—The author indicates a process which resolves itself into three phases:—A. The phosphorite is opened up with sulphuric acid, which must be in greater excess when the proportion of ferric oxide is small. In this case the excess of sulphuric acid is saturated with ferric hydroxide, which is obtained as a by-product in the further course of the process. The solutions must be kept very concentrated. B. The solution of ferric phosphate in ferric sulphate obtained in this manner is mixed with a sufficiency of water to throw down a considerable quantity of ferric phosphate. Complete precipitation would be disadvantageous, on account of the large quantity of water needful. The mother liquors are mixed with fresh portions of the crude material with the addition of more sulphuric acid. In case of ground basic slags, the solution must be more concentrated than for other materials, on account of the more abundant formation of crystallised gypsum. C. The ferric phosphate is decomposed with potassa-lye. In view of the improved electric process for the production of potassium hydroxide, its employment does not seem to be excluded. If an apparatus for dialysis should work successfully on the large scale, the ammoniacal solution of the ferric phosphate might be dialysed up to the point when the diffusion of the ammonium phosphate ceases, and the undecomposed ferric phosphate might be treated with potassa-lye.

Complex Inorganic Acids.—F. Kehrmann.

Phosphoduodecimolybdic Acid and Phospholuteomolybdic Acid.—(Experiments by E. Bohm).—The results, showing the action of the acids with the saline solutions of metals and organic bases, are given in the form of three tables.

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.

Tests for Morphine in Urea.—Will some correspondent kindly intimate the best source for obtaining information as to the most delicate tests for morphine in urea.—A. R. P.

MEETINGS FOR THE WEEK.

Monday, 20th.—Society of Arts, 8. (Cantor Lectures). "Japanese Art Industries," by Ernest Hart, D.C.L.
— Medical, 8.30. (Annual Oration).
Tuesday, 21st.—Royal Institution, 3. "Thirty Years' Progress in Biological Science," by Prof. E. Ray Lankester, F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30. (Anniversary).
— Society of Arts, 8. "Commercial Education in Belgium," by Prof. William Layton.
Wednesday, 22nd.—Society of Arts, 8. "The Dressing and Metallurgical Treatment of Nickel Ores," by A. G. Charleton, A.R.S.M.
— Geological, 8.
Thursday, 23rd.—Royal Institution, 3. "The Instruments and Methods of Spectroscopic Astronomy," by William Huggins, D.C.L., F.R.S.
— Society of Arts, 4.30. "The Northern Balochis—their Customs and Folklore," by Oswald V. Yates.
— Institute of Electrical Engineers, 8.
Friday, 24th.—Royal Institution, 9. "The Absolute Measurement of Electrical Resistance," by J. Viriamu Jones, F.R.S.
— Physical, 5. "On Mixtures of Ethane and Nitrous Oxide," by Dr. Kuenen. "The Measurement of Cyclically varying Temperature," by H. F. W. Burstall.
Saturday, 25th.—Royal Institution, 3. "Picture Making," by Seymour Lucas, A.R.A.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1852.

FORMIC ALDEHYD: ITS DETECTION IN MILK, AND VALUE AS A PRESERVATIVE.

By R. T. THOMSON, F.I.C.

The commercial form of this article, known as formalin, may be obtained for chemical purposes as a liquid guaranteed to contain 40 per cent of real formic aldehyd; but a much weaker solution appears to be sold to some extent to milk dealers for adding as a preservative to milk, in place of boric acid or borax.

As formic aldehyd requires to be added to milk only in very small quantity, it is evident that its detection, and especially its estimation, presents unusual difficulties. I have recently made experiments with the object of proving the presence of this substance in milks, and have found that a modification of the well-known reaction with ammonia-nitrate of silver gives a good indication of its presence. To apply the test 100 c.c. of the milk are carefully distilled until (say) 20 c.c. of distillate comes over: this is transferred to a stoppered tube, and about 5 drops of ammonia silver nitrate added. (This solution is prepared by dissolving 1 grm. of silver nitrate crystals in 30 c.c. of distilled water, adding dilute ammonia till the precipitate at first formed is re-dissolved, and then making up to 50 c.c. with water). The mixture of the milk distillate and the silver solution is now allowed to stand for several hours in a dark place (as much as twelve to eighteen hours may be necessary if very little formic aldehyd is present), when, if formic aldehyd is present, a strong black colour or deposit will be produced. A light brown colour should be disregarded; but, so far as my experience goes, the production of a decided black nnder these circumstances is only brought out by formic aldehyd, but possibly by other aldehyds also. The usual method of heating with the silver solution in order to obtain a silver mirror is of no value with weak solutions of formic aldehyd. It was found that genuine milks from various sources, when tested by the method described, gave no reaction whatever, even when the distillate was left mixed with the silver solution for twenty-four hours; or at most gave a slight brown tinge. When as little as 2 grains of the 40 per cent formalin was added to 1 gallon of milk (which before addition gave no reaction with this process), the distillate from 100 c.c. gave a decided black colour, or deposit intense enough to render the mixture quite opaque. As 2 grains per gallon is a quantity of formalin which would be of little value in the preservation of milk, it is evident that this method of testing is quite delicate enough for the purpose. It ought to be noted that, if a milk contains about 2 grains of formalin per gallon, the 20 c.c. distillate from 100 c.c. of the milk appears to contain all the formic aldehyd that will distil over, and distillates after that give practically no reaction. A milk containing 7 or 8 grains per gallon of the preservative may require the distillation to be carried on till 30 or 40 c.c. are collected, before it ceases to show a reaction with the silver solution; but in all cases the reaction can be got by distilling over the 20 c.c., or indeed 10 c.c.

An attempt was made to determine the proportion of formic aldehyd in a milk by comparing the depth of colour obtained from its distillate with that given by a standard solution of the aldehyd. This was not successful, owing to the fact that the reduced silver often forms a deposit on the side of the tube, while the liquid is comparatively colourless. In this connection it was noticed that the distillate from a milk containing a certain proportion of formic aldehyd did not give nearly so great a depth of black colour as the same amount simply added to water, and then tested with the silver solution. This would point to the conclusion that there is a loss of formic aldehyd, probably by decomposition, during the distillation, and this also would add to the incorrectness of a determination.

I should have mentioned that care should be taken not to add excess of ammonia to the ammonia silver nitrate solution used in the test, as if much excess of ammonia is present no reaction will be obtained, even in presence of formic aldehyd.

It has been mentioned by other chemists that formalin may be used as a preservative for milk samples; and I have found by experiment that samples, to which has been added 4 or 5 drops of the 40 per cent formic aldehyd per 100 c. c. of the milk, have kept in good condition for six weeks, and given the same results, on analysis after that period, as when analysed before the preservative was added. As formic aldehyd is in such an available form for addition to milk samples, without in any way interfering with the accuracy of the results of analysis, it should prove useful to analysts in the preservation of samples for reference. As in the case of other preservatives, its use for milk supplies should not be recommended until its harmlessness were fully proved.

I have also made a few experiments with the view of comparing the value of formic aldehyd as a preservative with such well-known articles as boric acid, salicylic acid, and benzoic acid. For this purpose measured quantities of the same milk, to which the various preservatives were added, were kept in stoppered bottles under the same conditions as nearly as possible, and the condition of each examined from time to time, one sample of the milk free from preservative being also kept along with these for comparison. In the following Table will be found the results of the observations made:—

Table showing the Preserving Power, as regards Milk, of Certain Preservatives.

Preservative employed.	Milk after standing 6 days.	Milk after standing 7 days.	Milk after standing 8 days. Lactic acid per cent.	Milk after standing 11 days. Lactic acid per cent.
None	Sour	Sour, curdled	0·68	0·71
40 p.c. formic aldehyd (8¾ grs. per gall.)	Sweet	Sweet	0·12	0·43
40 p.c. formic aldehyd (17½ grs. per gall.)	Sweet	Sweet	0·10	0·14
40 p.c. formic aldehyd (35 grs. per gall.)	Sweet	Sweet	0·07	0·10
Boric acid (35 grs. per gall.).. ..	Turned	Sour, curdled	0·42	0·52
Boric acid and borax in equivalent quantities (= 35 grains boric acid)	Sweet	Sweet	0·10	0·32
Salicylic acid (35 grs. per gall.)	Sweet	Sweet	0·10	0·33
Benzoic acid (17½ grs. per gall...	Slightly turned	Sour	0·45	0·52

It is apparent from these results that 8¾ grains of the 40 per cent solution of formalin are quite as effective in preserving milk as four times that amount of boric acid (at least when used as a mixture of boric acid and borax), and the same proportion of salicylic acid, while the preserving power of benzoic acid is very low compared with what might be expected from statements made in text-books. It also seems peculiar that boric acid alone is much inferior to a mixture of boric acid and borax, so made up that each of these substances contributes equal to 17·5 grains of crystallised boric acid per galion of milk. The proportion of 35 grains of boric acid per gallon of milk was adopted because that is about the usual amount I have found in samples to which that preservative had been added.

It may quite reasonably be argued that the results given above are not sufficient in number to allow of any decided opinion as to the exact comparative value of the preservatives tested; but, taking into consideration the concordant results of the three tests with formic aldehyd, I have no hesitation in claiming that these are approximately the values of the respective preservatives for milk at least.

I am continuing my experiments with formic aldehyd, in order to find a method of determining the amount present in a milk, as well as its value in preserving milk samples, and also further and extended experiments on the value of the various preservatives.

City Analysts' Laboratory, Glasgow.

SODIUM BISULPHITE.

By R. E. EVANS and C. H. DESCH.

During the severe weather experienced during the early part of this year a great number of compounds crystallised out from solutions which at ordinary temperatures have no tendency in this direction. The following account of a compound obtained in this manner may be of interest, as it has not been previously described.

A quantity of about 95 gallons of bisulphite of soda solution, of sp. gr. 1290, was left exposed for several days during the most severe frost, and on running off the liquid the sides of the vat were found to be incrusted with large glittering crystals, the total quantity of which must have exceeded 2 cwt. They were very regular in shape, and, exposed to the air, tended to effloresce with a faint smell of sulphurous acid.

Analysis gave the following results:—

	Crystals.	Calculated for $Na_2SO_3SO_2+7H_2O$.
Na_2O	20·01	19·56
SO_2	39·81	40·50
Na_2SO_3	40·66	39·87
SO_2	19·16	20·26
H_2O	40·18	39·87

The compound was therefore crystallised bisulphite of soda, with 7 molecules of water of crystallisation. A considerable quantity of the crystals were stored in a well-stoppered bottle, but in a short time, as the weather became warmer, they partly deliquesced, forming a semi-fluid mass, consisting of fine pearly white crystals suspended in a heavy fluid. These were filtered off, and drained as far as possible by pressure between filter-paper. They gave off SO_2 rather strongly, and the analysis was therefore performed at once, and the remaining moisture (2·5 per cent) was allowed for in the calculations:—

	Crystals.	Calculated for $Na_2SO_3SO_2$.
Na_2O	32·74	32·63
SO_2	67·26	67·37
Na_2SO_3	66·37	66·31
SO_2..	33·63	33·69

There can be no doubt, therefore, that this salt was anhydrous bisulphite of soda. The gravity of the liquid portion was 1164·98, and consisted of a solution of the bisulphite,

It is evident, therefore, that by intense cold a very well-crystallised form of bisulphite of sodium may be obtained containing 7 molecules of water; and this is readily given up, even in a closed space, with formation of the more stable bisulphite.

The Laboratory, Stratford-on-Avon.

ARGON IN MINERALS.

We have received a letter from Professor W. R. Eaton Hodgkinson from which we extract the following interesting observations:—

"I have obtained from certain minerals gases which seem to contain argon, and perhaps also helium. Minerals of the samarskite group when heated to some particular temperature commence to glow, and this appearance has hitherto been ascribed to a molecular re-arrangement. As I could not find any account as to whether the weight was in any way changed in this action, I have recently, with my assistant, Mr. Young, A.R.S.M., heated euxenite and samarskite *in vacuo* and extracted the gases. At the moment of glow a large quantity of gas—twelve times the volume of the mineral —is given off. This gas we have sparked, and the colour and spectrum point to a hydrocarbon being present. On adding oxygen to the gas and exploding, there is a decided contraction, and after introducing potash a further greater contraction. After the excess of oxygen is absorbed the spectrum is no longer like a hydrocarbon, but has a close resemblance to the argon spectrum, according to the published accounts. We have so far obtained the same results from euxenite as from samarskite."

ON THE PHOTOGRAPHY OF THE RAYS OF SMALLEST WAVE-LENGTH.*

By VICTOR SCHUMANN.

Previous experiments which I had performed with strata of air up to 1 m.m. in thickness had shown that the photography of the light rays below the wave-length 185 $\mu\mu$ required the exclusion of air from the track of the rays. Under these circumstances, an essential extension of the spectrum of the air beyond the wave-length 185 $\mu\mu$ seemed impracticable. But, according to my most recent experiments, very thin strata of air, such of about 0·1 $\mu\mu$ in thickness, transmit a great part of the rays of the smallest wave-lengths, and strata whose thickness does not exceed a few hundredths of a m.m. seem merely to check, but not to quench, the energy of the rays. With the former the photograph extends far beyond 162 $\mu\mu$, the locality of the photographic maximum of hydrogen; whilst with the latter we are able to proceed considerably further. Indeed, according to all appearance, these, if only exposed for a sufficient time, may present no important hindrance to attaining the actual limit of the region of the smallest wave-lengths.

From this fact, which I have repeatedly verified, I believe that I can deduce a result concerning the photography of the smallest wave-lengths totally unexpected in accordance with my earlier observations. I employ a discharging tube, so constructed that it may be connected air-tight with the exhausted spectrograph in a manner suitable for photographic application, and thereupon, independently of its vacuum, can be filled with any required gas at any given pressure. The tube and the spectrograph, therefore,—in an essential contrast with my former experimental arrangement—were not in conductive connection. This discharging-tube, differing in form and arrangement from my previous arrangements of this kind, presents, along with other advantages, one which comes exclusively into consideration in the present case, *i.e.*, that the resistance of absorption which the rays encounter by the contained gas can be reduced without difficulty to an extremely small quantity by a decrease of pressure and depth of stratum.

I purpose subsequently to communicate further par-

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* Imperial Academy of Sciences at Vienna, Session of the Class of Mathematics and Natural Science, April 25, 1895.

ticulars with my photographs—now in course of execution—of the ultra-violet spectrum of hydrogen.

With such a tube I now obtained, after it has been filled with dry air at a low pressure, the spectrum of the air as an extremely energetic band of efficacy, of a wavelength hitherto not attained, which closely approximates, in photographic energy and extent, to the most effective of all the ultra-violet spectra hitherto known, that of hydrogen. For instance, the most effective region of these pictures presents in a length of 34 m.m. more than fifty bands, partly resolved into lines shading away towards the red, and following upon each other so closely that in their totality they appear to the naked eye as a continuous effective band of varying density. To what constituent of the atmosphere these bands belong future observations must decide.

VARIATION IN THE AMOUNT OF FREE AND ALBUMENOID AMMONIA IN WATERS, ON KEEPING.

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

(Concluded from p. 237).

Table VII.

About 1 grm. of White of Egg was diffused as uniformly as possible, first through a small quantity and then through a larger volume of Distilled Water, and nine quart bottles filled up with the mixture.

Temp. °F.				Free NH_3.	Alb. NH_3.
Morn.	Even.	Nos.	Date.		
72	72	1	Nov. 24	0·33	0·37
66	69	2	,, 27	0·33	0·49
66	68	3	,, 29	0·50	0·56
67	68	4	,, 30	0·40	0·60
68	68	5	Dec. 1	0·40	0·70
66	71	6	,, 4	0·60	0·70
73	73	7	,, 6	0·60	0·77
76	77	8	,, 7	0·60	0·72
77	78	9	,, 8	0·50	0·80

It will be noticed in the above table that the amounts of both free and albumenoid ammonia increased very greatly after four or five days, showing that the fresh albumen, like urine, does not yield ammonia so readily as that which is more or less decomposed; as the amount of albumenoid ammonia had increased in the ninth and last bottle, a larger series would have been more satisfactory.

Table VIII.

Eight Bottles each of Garden Tank Water and NH_4NO_3 and Distilled Water and NH_4NO_3.

(Rained heavily for 24 hours before putting up this series).

Temp. °F.				Garden Tank Water and NH_4NO_3.		Distilled Water and NH_4NO_3.	
Morn.	Ev.	Nos.	Date.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.
75	76	1	Nov. 17	0·46	0·09	0·40	0·09
75	76	2	,, 23	0·36	0·05	0·32	0·05
66	69	3	,, 27	0·04	0·05	0·30	0·09
68	69	4	,, 28	0·03	0·04	0·48	0·11
66	68	5	,, 29	0·03	0·04	0·48	0·07
67	68	6	,, 30	0·03	0·04	0·40	0·11
68	68	7	Dec. 1	0·03	0·04	0·48	0·11
66	71	8	,, 4	0·02	0·04	0·50	0·09

It will be noticed that the distilled water containing ammonium nitrate yielded nearly equal amounts of free and albumenoid ammonia all through the series, but the mixture of ammonium nitrate and garden tank water soon showed a rapid diminution in the amount of ammonia. The great change which had taken place was probably due to the fermentation or decomposition of organic matter in the tank water or to the action of organisms, or perhaps to both. The amounts of albumenoid ammonia were small throughout, but larger than those yielded by the other series of garden tank water.

Table IX.

Ten Bottles each of Horse Pond and Fish Pond Waters, undiluted.

Temp. °F.				Horse Pond.		Fish Pond.	
Morn.	Ev.	Nos.	Date.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.
73	75	1	Dec. 11	10·00	7·00	0·12	0·90
77	78	2	,, 12	2·00	2·00	0·11	0·92
71·5	73	3	,, 13	8·00	4·00	0·16	1·04
76	78	4	,, 15	7·00	4·00	0·16	1·03
80	78	5	,, 16	6·00	2·00	0·38	0·69
74	75	6	,, 19	5·00	2·00	0·52	0·56
76	77	7	,, 20	4·00	1·00	0·70	0·38
75	76	8	,, 21	2·00	0·50	0·90	0·30
			1877.				
75	75	9	Jan. 8	0·50	0·25	1·38	0·06
73	74	10	,, 10	0·07	0·07	1·50	0·04

Note.—On account of the large quantity of organic matter present in the horse pond water, 10 c.c. only of it was used for each determination; this was made up in the retort to 500 c.c. by the addition of distilled water free from ammonia.

Table X.

Seven Bottles each Garden Tank and Peaty Water and Garden Tank and Ammonia Solution.

Temp. °F.				Garden Tank and Peaty matter.		Garden Tank and Free NH_3.	
Morn.	Ev.	Nos.	Date.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.
73	75	1	Dec. 11	0·72	0·19	2·8	0·20
77	78	2	,, 12	1·12	0·04	2·80	0·20
71·5	73	3	,, 13	1·12	0·13	2·72	0·23
76	78	4	,, 15	1·08	0·12	2·70	0·21
80	78	5	,, 16	0·03	0·04	0·64	0·10
74	75	6	,, 19	0·02	0·03	0·56	0·07
76	77	7	,, 20	0·01	0·01	0·20	0·01

The self purification of the above samples is very remarkable.

DETECTION AND ESTIMATION OF SELENIUM IN METEORIC IRON.

By H. N. WARREN, Research Analyst.

The following is an outline of the analysis of several specimens of meteoric iron which have been lately brought before my notice, and which, during the course of analysis, were all more or less found to contain small quantities of selenium associated with the iron, the separation of which was effected as follows:—

By reducing 10 grms. of the specimen to a rough powder by filing, and intimately mixing it with pure flour of sulphur in sufficiency, the whole being introduced into a stout piece of combustion tubing and heated to redness. One end of the tube is in connection with an apparatus evolving oxygen gas, for the purpose of burning off the sulphur, forming sulphurous anhydride, and expelling with it the small quantity of selenious anhydride formed at the same time by the combustion of the selenium present. The further end is connected with a series of bulb tubes containing distilled water to collect the reduced selenium formed by the action of the sulphurous acid produced. The solution containing the precipitated selenium is next

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* Read before the Australasian Association for the Advancement of Science, Brisbane, January, 1895.

heated to a temperature of 80° F., to render it more dense, introduced into a platinum dish, dried in the air-bath, and weighed (a blank estimation being in each case determined with the sulphur employed). A tabulated view is appended of the meteoric iron whem separated from the matrix. A, B, from Bohumilitz; C, Pallus iron; D, Elbogen; E, F, Atacama Desert.

	A.	B.	C.	D.	E.	F.
Iron	90·10	94·51	95·04	88·20	70·01	86·52
Nickel . ..	6·54	2·54	3·20	8·20	20·02	10·52
Cobalt . ..	0·24	0·32	0·12	0·12	—	0·12
Copper ..	—	—	0·20	—	—	—
Manganese .	0·12	—	0·12	0·23	—	—
Selenium ..	0·23	0·050	0·04	0·06	0·08	0·05

Liverpool Research Laboratory,
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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 APRIL 30TH, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 8th, 1895.

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 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 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 168 samples examined two were recorded as "clear but dull," the remainder were clear, bright, and well filtered.

The London waters have now assumed the high degree of purity which we are accustomed to observe during the summer when the activity of fluviatile vegetation, unduly kept back during the abnormally low temperature of the last few months, is fully at work, oxidising and transforming the dissolved organic matter and lowering the colour. In chemical composition the analyses show almost the same results as were obtained last month, a slight improvement being seen in common salt, hardness, nitric acid, and colour.

Bacteriologically the filtered waters from the general wells at the works contained an average of 46 microbes per c.c., while the unfiltered water contained 9175 per c.c., showing a filtration efficiency of 99·5 per cent.

The rainfall at Oxford has been identical with the average for 25 years, being in each case 1·78 inches. Of this amount more than one-third fell on the 25th inst.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

A NEW CLASS OF COMPOUNDS OF THE INACTIVE HYDROCARBONS.

No. II.

By J. ALFRED WANKLYN and W. J. COOPER.

In the Chemical News (vol. lxx., p. 211) we published a note with the above title, explaining that the thermal phenomena attendant on the mixture of the hydrocarbons of Russian kerosene with glacial acetic acid point to the conclusion that these hydrocarbons enter into chemical combination with acetic acid.

We have continued the investigation, which bears out this conclusion most completely.

In the first place it has become quite clear that one molecule of each hydrocarbon enters into chemical combination with one molecule of the fatty acid, forming a liquid compound endowed with sufficient stability to admit of its being purified and handled, and analysed in a thoroughly satisfactory manner. We have obtained the acetic combination with each one of seven consecutive terms of the kerosene series, the analyses of which we give:—

		Percentage of Hydrocarbon.	
		Theory.	Found.
xiv.	*$C_{14}H_{14},C_4H_4O_2$	62·04	62·33
xv.	$C_{15}H_{15},C_4H_4O_2$	63·63	62·75
xvi.	$C_{16}H_{16},C_4H_4O_2$	65·12	64·48
xvii.	$C_{17}H_{17},C_4H_4O_2$	66·48	65·9 (mean)
xviii.	$C_{18}H_{18},C_4H_4O_2$	67·74	67·85
xix.	$C_{19}H_{19},C_4H_4O_2$	68·91	69·06
xx.	$C_{20}H_{2c},C_4H_4O_2$	70·00	69·70

The analyses were made by taking advantage of the circumstance that all of these acetic combinations with the hydrocarbons are readily decomposed by water. A comparatively large quantity of the acetic compound was employed—from 30 to 120 grms.: this was treated with water and washed thoroughly, and the resulting oily hydrocarbon was weighed. The results, as will be seen, are perfectly satisfactory.

The preparation of the compounds is very simple, and, with one exception, the compound is very readily obtained in a fairly pure condition.

The hydrocarbon is mixed with a moderate excess of glacial acetic acid, and, when necessary, gently warmed. Two layers of liquid are formed, the upper and larger layer being the compound which is sought, and the lower being acetic acid holding some of the acetic compound in solution. A glass stop-funnel is used in order to separate the two layers of liquid. Instead of taking only a moderate excess of the acid, a large excess—that is to say, more than twice the theoretical quantity of acid—may be taken. In that case the addition of a minute quantity of water, amounting to about 0·1 c.c. to 25 c.c. of the acid, may be resorted to in order to remove the excess of acetic acid. A similar result is arrived at by adding a very small quantity of formic acid.

As has been said, we have experienced no difficulty in preparing six of the seven acetic compounds the formulæ of which have been set out. The exception is the compound of kerose (xvii.), which is not easily obtained pure; and the analytical figure in our tabular statement (as we have indicated) is the mean of nine analyses of different specimens produced in a variety of ways.

The compounds present many points of interest; they distil, with at least partial decomposition, at singularly low temperatures, as we pointed out in our former paper. At low temperatures, too, they appear partially to decompose into fatty acid and hydrocarbon, thus:—

Kerose. Acetic Acid.

$$2(\mathrm{keC_4H_4O_2}) = 2\mathrm{ke} + \left.\begin{array}{l} C_4H_4O_2 \\ C_4H_4O_2 \end{array}\right\}$$

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* In this paper the atomic weight of carbon is written 6.

The explanation of the change is, that the small single molecules of acetic acid in combination with the kerose are very prone to combine with themselves to produce the double molecule of liquid or solid acetic acid.

Extending our enquiry to other members of the fatty acid family, we have observed that formic acid behaves quite differently from acetic acid. It appears to be quite incapable of forming these compounds.

Butyric acid and valerianic acid, on the other hand, form them quite readily.

Kerose xv. has given a compound with butyric acid yielding 53·10 per cent of the hydrocarbon. The theory for $C_{15}H_{15}C_8H_8O_2$ requires 54·40 per cent of $C_{15}H_{15}$.

Kerose xvii. has given the valerianic compound $C_{17}H_{17}C_{10}H_{10}O_2$, yielding 54·82 per cent of $C_{17}H_{17}$, the theory requiring 53·85.

Kerose xix. has given $C_{19}H_{19}C_{10}H_{10}O_2$, yielding 56·48, the theory requiring 56·60 of hydrocarbon.

The butyric compound was prepared like the acetic compounds, viz., by mixing the hydrocarbon with a moderate excess of the acid, and allowing the excess of acid to separate out as a lower layer of liquid.

The valerianic compounds were prepared somewhat differently. Valerianic acid was added to about its own volume, or rather more than its volume, of formic acid (with which it formed a perfectly homogeneous mixture), and then the hydrocarbon was poured in, considerably less than the theoretical quantity of hydrocarbon being employed. Under these circumstances the hydrocarbon seizes hold of its equivalent of valerianic acid, and forms the liquid valerianic compound, the formic acid playing the part of solvent medium. Here are the details of the experiment from the note-book:—

20 c.c. of valerianic acid mixed with 25 c.c. of formic acid, and then 20 c.c. of the kerose added. An upper layer of liquid, measuring 32 c.c., separated and washed with two small relays of formic acid, 2 c.c. and 3 c.c. respectively. Ultimate volume of the valerianic liquid, 31 c.c.

25·843 grms. taken for analysis and decomposed with weak ammonia, and the resulting hydrocarbon was washed and weighed. 14·695 grms. ∴ Oil = 56·48 per cent. Theory 56·60.

The valerianic compounds would seem to have more stability than the acetic compounds, inasmuch as they admit of being placed in contact with more than as much formic acid as valerianic acid *in the process of their formation.*

In the case of the acetic bodies only traces of formic acid are admissible in admixture with the excess of acetic acid. We are continuing the work.

Laboratory, New Malden, Surrey,
May 20, 1895.

ON GOLD SULPHIDE.

By A. DITTE.

The action of a current of hydrogen sulphide upon a dilute solution of gold chloride varies according to circumstances. If the liquid is neutral the first bubbles of the gas occasion a brown colouration, which deepens as the current passes, and when it is saturated it gives no deposit of a metallic sulphide. The solution is then deep brown, transparent, and passes through filters without losing any of its colour. I then left it to itself, in a closed vessel, at the ordinary temperature; it is slowly modified.

The gold sulphide is transformed in the course of twenty-four hours, or of a longer time; the liquid is still dark, but it is decolourised on filtration, or if left alone it slowly deposits gelatinous gold sulphide, which on agitation with water remains for a long time in suspension, forming a coloured liquid. The addition of a few drops of hydrochloric acid to the dark solution which passes through the filters, or to that which holds the gelatinous precipitate in suspension, rapidly causes the deposition of gold sulphide in the form of a black powder, and the liquid becomes colourless. This condition is reached at once if a currrent of hydrogen sulphide is passed into an acid solution of gold chloride.

Gold sulphide may thus take very different aspects from the soluble matter produced in a neutral solution, or obtained, as by Schneider, on dialysing a solution of gold cyanide in potassium cyanide saturated with hydrogen sulphide (*Berichte*, xxv., p, 2241) up to the dense black sulphide insoluble in water. This sulphide, if brought in contact with an alkaline sulphide, occasions various reactions.

If we gradually add sodium monosulphide to the black insoluble gold sulphide it gradually dissolves, and an excess of alkaline sulphide gives an orange-red solution having the odour peculiar to solutions of the alkaline persulphides.

This solution, if slowly evaporated in a vacuum, deposits aggregations of crystals formed by colourless transparent crystals radiating around a point. If well dried on porous porcelain their composition may be represented by the formula $Au_2S,2Na_2S,20H_2O$. These crystals blacken on the surface under the action of organic substances. They are very soluble in water, forming a colourless liquid in which dilute acids give at once a precipitate of gold sulphide.

If the alkaline sulphide is only in very slight excess we obtain an orange-yellow liquid, which in a vacuum deposits fine needles of the double sulphide,—

$$Au_2S,Na_2S,10H_2O,$$

and the mother-liquor on further concentration yields a supersaturated solution, which sometimes coagulates in a mass, and sometimes deposits small prisms, short, deliquescent, not containing gold, very soluble in water, yielding a yellow liquid in which dilute acids give an abundant deposit of sulphur. They consist of hydrated bisulphide, $Na_2S_2,8H_2O$.

Thus, on contact with sodium monosulphide in excess, gold sulphide passes into the state of aurous sulphide, Au_2S, which combines with the alkaline sulphide to form double sulphides, soluble in water without decomposition, whilst the sulphur set at liberty forms sodium bisulphide.

It is otherwise if the gold sulphide is in excess. A certain quantity dissolves, and then the undissolved portion decreases in volume, changes its colour, and after some days is converted into a dense, dull, greenish-yellow powder, formed of very minute crystals adhering together and opaque. This substance contains no sulphur; it is pure gold crystallised in the moist way. The small proportion of alkaline sulphide placed in contact with the excess of gold sulphide forms at first a double sulphide and sodium bisulphide. The latter continues to remove sulphur from the gold sulphide, setting the metal at liberty until the alkaline persulphide is saturated with sulphur. Lastly, the double sulphide in contact with excess of gold sulphide is decomposed and changed into alkaline persulphide depositing aurous sulphide. If, when all the alkaline sulphide is saturated with sulphur, there still remains gold sulphide undecomposed, it undergoes no further modification, the alkaline persulphide having no action upon it.

The gold sulphide, in fact, does not appreciably dissolve in a solution of sodium sulphide saturated with sulphur. On the other hand, a solution of gold sulphide in an excess of alkaline monosulphide, with the addition of fragments of sulphur, gives rise to the formation of a deposit of black sulphide, which increases in proportion as the sulphur dissolves, and when the liquid is saturated it contains merely traces of gold. Finally, the gold liberated does not give rise to any inverse reaction, for gold-leaf left for eighteen months in contact with a solution of sodium sulphide saturated with sulphur, at the ordinary temperature and in a sealed tube, is not affected by this liquid.

If for sodium sulphide we substitute that of potassium we observe analogous facts, but potassium sulphide—much more soluble in water than sodium sulphide—gives rise to double salts much more soluble in water than those formed with sodium, and more difficult to isolate in a state of purity. If we dissolve gold sulphide in a very slight excess of potassium sulphide we most frequently obtain a residue of metallic gold on operating in the cold, or at 30° to 40°. The filtered liquid, if evaporated in a vacuum, becomes a thick red syrup, ultimately depositing crystals. The crystals may be freed from their mother-liquor by depositing them upon a plate of very dry porcelain protected from moisture. The crystals are gold-coloured needles, very deliquescent, and very soluble in water, to which they give a yellow colour. If exposed to light they turn grey on the surface, and their composition may be represented by $Au_2S,4K_2S_2,12H_2O$. The mother-liquor coagulates into a mass on concentration *in vacuo*, whilst no definite compound is separated.

Potassium monosulphide in contact with an excess of gold sulphide deprives it of sulphur and separates metallic gold, exactly as takes place with sodium sulphide. The potassium sulphide saturated with sulphur has, like the sodium compound, no action in the cold, either upon gold sulphide or upon metallic gold. — *Comptes Rendus*, cxx., p. 320.

ON THE ADDITION OF ANILINE AND PHENYLHYDRAZIN TO BENZALMALONIC ESTER.

By R. BLANK.

Alkylidenmalonic esters have as yet been examined only slightly, and in a desultory manner, but in almost every investigation there was discovered a new remarkable additive reaction of the compounds of this type (general formula $R.CH:C(CO_2R_2)$).

Thus, Zalinsky observed that methylenmalonic ethylester is polymerised to a dimolecular compound, with a liberation of heat.

On saponifying this ester with potassa-lye he obtained the addition-compound of the corresponding acid with 1 mol. of water, whilst Tanator arrived, on using alcoholic potassa, at taradipimalic acid, the addition-product of the acid with 1 mol. of alcohol. A similar additive reaction was discovered by Claisen and Crismer on saponifying benzalmalonic ethyl ester with alcoholic potassa. On saponifying benzalmalonic methylester with methylic potassa there occurs an addition of water.

Ethylidenmalonic ester unites at a boiling heat with 1 mol. of malonic ester.

Finally, C. Liebermann demonstrated in an entire series of alkylidenmalonic esters the power of taking up additionally 1 mol. of sodium methyl (or ethyl) alcoholate.

I have now observed that the addition of aniline and phenylhydrazin to benzalmalonic ester takes place quite as smoothly.

Addition of Aniline to the Acid Benzalmalonic Methylester.

On adding 1 mol. aniline to the concentrated solution of the above acid ester in benzene there is formed, not the corresponding aniline salt, but an addition-compound of this salt with aniline, whence we may infer that the tendency of the ester-acid (or of its salt) to the addition of aniline is at least as great as its disposition to form a salt with the same base.

The subsidence of the compound begins soon after the ingredients have been brought into contact; it increases very slowly, and is quite considerable after two or three hours. A considerable part, however, remains in solution in which is retained the unconsumed part of the ester-acid. A further quantity of the compound may be precipitated by a further addition of aniline to the mother-liquor.

The new compound was washed with benzene, dried in a vacuum exsiccator over paraffin and sulphuric acid, and gave on analysis a composition corresponding to—

$$C_{23}H_{24}N_2O_4.$$

It has the form of white felted needles, melting at 97·5°; it is insoluble in water, but readily soluble in the ordinary organic solvents except ligroin. In dilute hydrochloric acid it forms at first a clear solution, which soon becomes turbid and gives off a smell of benzaldehyd. The same odour is perceptible if it is exposed to moist air.

According to analogy, with the additive reactions mentioned above, in which an easily mobile atom of hydrogen (or sodium) passes to the α-atom of carbon, whilst the residue attaches itself to the β-atom of carbon, we must regard the aniline addition-compound as an aniline salt of the β-anilidobenzylmalonic monomethyl ester, which is confirmed by the solubility of the compound in hydrochloric acid.

Addition of Aniline to the Neutral Benzalmalonic Methyl Ester.

β-Anilidobenzylmalonic methyl ester,—

$$C_6H_5.CH(NHC_6H_5).CH(CO_2CH_3)_2.$$

The ester is dissolved in a little benzene, and to the cold solution there is added 1 mol. of aniline. On the mixing, heat is liberated, and after standing at the common temperature for three or four hours the solution congeals to a white crystalline cake. The crystals are ground up and dissolved in a little benzene. If the cold solution is mixed with three vols. of ligroin, fine needles separate out, fusible at 117—118°.

For analysis the preparation was re-crystallised in the same manner and dried as above over paraffin and sulphuric acid in the vacuum exsiccator. Its composition is $C_{18}H_{19}NO_4$.

The same compound is formed by the reaction of two mols. aniline with one mol. of the ester. It is readily soluble in the ordinary organic solvents, except ligroin. In water it is insoluble. It dissolves in strong hydrochloric acid, but is precipitated unaltered on the addition of water.

The hydrochlorate is easily isolated; the anilidobenzylmalonic ester is dissolved in anhydrous ether, and a current of dry hydrochloric gas is passed into the solution.

In about half an hour the finely crystalline salt is filtered off, washed with ether, and dried in the exsiccator. The salt is very unstable, and loses hydrochloric acid on standing over soda-lime. On standing with water it is decomposed quantitatively into anilidobenzylmalonic ester and hydrochloric acid. After filtering off the ester, the hydrochloric acid in the filtrate may be determined as silver chloride. The composition of the salt is $C_{18}H_{19}NO_4.HCl$.

β-Phenylhydrazidobenzylmalonic methylester,—

$$C_6H_5.CH(NH.C_6H_5).CH(CO_2CH_3)_2.$$

This compound is formed under the same conditions as the aniline compound just described, which it resembles in its external aspect and in its relations of solubility. Its melting-point is at 94·5°. Its composition is $C_{18}H_{20}N_2O_4$.

If melted in a dry state, or if boiled in solution in absolute alcohol, it splits off malonic ester and is transformed into benzylidenhydrazon which melts at 157°, and on the addition of ferric chloride to its solution in concentrated sulphuric acid takes the well-known blue colour.

Benzylidenhydrazon has been recently obtained by Wislicenus on boiling benzalmalonic ester with phenylhydrazin in solution in absolute alcohol. The reaction may be conceived of as expulsion of malonic ester by phenylhydrazin.

The reaction occurs in two phases, the addition-compound obtained in the first phase being in the second split up into benzylenhydrazon and malonic ester.

Additive reactions between amines and non-saturated acids have been repeatedly observed, such as the addition of aniline to maleïc acid by Anschütz, and that of phenylhydrazin to maleïc and fumaric acids by P. Duden.—*Berichte*, xxviii., No. 2, 1895, p. 145.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 2nd, 1895.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Messrs. Vaughan Cornish, G. Cecil Jones, and Patrick H. Kirkaldy were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Morison, 7, O'Connell Street, Sydney, N.S.W.; Albert Joseph Simons, Elmhurst, New Barnet.

Of the following papers those marked * were read:—

*54. "*Studies on the Constitution of the Tri-derivatives of Naphthalene, No.* 10. *The Dichloro-α-Naphthols and Trichloronaphthalenes from* 3 : 4-*Dichlorophenyl*-1-*Isocrotonic Acid.*" By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

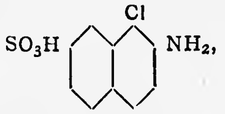
Having increased the number of known trichloronaphthalenes to 13 and determined their constitution (*cf. Proc. Chem. Soc.*, 1889, 48; 1890, 11, 84, 125 *et seq.*; 1891, 27; *B. A. Report*, 1891, 265), the authors naturally endeavoured to obtain the only remaining member of the series—the 1 : 2 : 1' trichloronaphthalene; and failing to prepare this by any of the ordinary methods, they turned their attention in the autumn of 1890 to the two dichloronaphthols described by Erdmann and Schwechten (*Annalen*, cclx, 78; *cf.* cclxxv., 286), one of which was necessarily the 1 : 2 : 1', and the other the 2 : 3 : 1' derivative, as both were formed on distillieg 3 : 4-dichlorophenyl-1-isocrotonic acid. But as their discoverers had not ascertained the exact constitution of either, it was necessory to examine both; and through the courtesy of Dr. Erdmann the authors were enabled to undertake their investigation: they ultimately succeeded in preparing the desired trichloronaphthalene from the dichloronaphthol of lower melting-point. Special care was taken to purify the materials used (*cf.* Wynne, *Trans. C. S.*, 1892, 1053), as no other case was known of two isomeric chloronaphthols being simultaneously formed on condensing a chlorophenylisocrotonic acid. The purified dichlorophenylparaconic acid melting at 138°, obtained from 1700 grms. of 1 : 3 : 4-dichlorotoluene, weighed 326 grms.; on converting it into the isocrotonic acid and distilling this acid, the two isomeric dichloro-α-naphthols were obtained in the proportion of about one part of that of the lower to two parts of that of the higher melting-point.

1 : 2 : 1'-dichloro-α-naphthol crystallises from dilute alcohol in slender, flat needles, 2—3 m.m. long; it melts at 95° (not 83°, as stated by Erdmann and Schwechten). Its acetate crystallises in long, flat needles, melting at 87—88° (not 71—72°). On distillation with phosphorus pentachloride it yields a mixture of tri- with some tetrachloronaphthalene, separable by crystallisation from methylic alcohol. The trichloronaphthalene thus obtained crystallises in long, slender needles melting at 83°; its identity with the 1 : 2 : 1'-compound prepared by Clève's method has been established by a careful comparison, by optical methods, of the two products.

2 : 3 : 1'-dichloro-α-naphthol melts at 151°, and has all the properties ascribed to it by its discoverers; on distillation with phosphorus pentachloride it also yields a mixture of tri- and tetra-chloronaphthalene, from which the former can be separated by fractional crystallisation from methylic alcohol. The trichloronaphthalene crystallises in microscopic needles melting at 109°, and has been identified by optical methods with the 2 : 3 : 1'-derivaiive of this melting-point first described by the authors in 1890 (*Proc. Chem. Soc.*, 1890, 83).

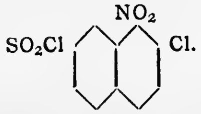
*55. "*Studies on the Constitution of the Tri-derivatives of Naphthalene, No.* 11. *The Trichloronaphthalene derivable from Clève's* 1 : 2 : 2'-α-*Nitrochloronaphthalenesulphonic Chloride.* By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

Of the three isomeric chloro-β-naphthylaminesulphonic acids described by the authors in their papers on the determination of the constitution of the heteronucleal di-derivatives of naphthalene (*Proc. Chem. Soc.*, 1889, 34 and 48), one (the so-called No. 3 acid) was shown to have the constitution—



and from this a dichloronaphthalenesulphonic chloride melting at 122—123°, and a trichloronaphthalene melting at 83—84°, were prepared, which presumably were also 1 : 2 : 2'-derivatives.

The important series of experiments on the nitration of the chloronaphthalenesulphonic chlorides carried out by Clève in 1892-93 includes the nitration of the 2 : 2'-derivative (*Ber.*, 1892, 2485; *Ofversigt*, &c., 1892, 417), from which he prepared a nitrochlorosulphonic chloride of the formula—



Although he obtained a dichloronaphthalenesulphonic chloride from this nitro-compound identical with that prepared by the authors from their No. 3 acid, yet by directly distilling the nitrosulphonic chloride with phosphorus pentachloride Clève obtained a product which he described as a trichloronaphthalene, which separated from alcohol in crystalline granules *melting at* 75·5°, and it was stated by him that this was identical with that prepared by Alén from α nitronaphthalene-2 : 2'-disulphonic chloride (see further). And in describing his method of preparing 1 : 2 : 1'-trichloronaphthalene shortly afterwards (*Ofversigt*, 1893, 81), Clève regarded the substance he obtained as identical with that prepared by the authors from their No. 3 acid; he does not appear to have made any direct comparison of the products from the two sources, however.

Comparing these observations together, as in the following Table, it is evident that either a remarkable isomeric change occurs when a dichlorosulphonic chloride, but not when a nitrosulphonic chloride, is distilled with phosphorus pentachloride, or Clève's conclusions are erroneous.

	$Cl_2 \cdot SO_2Cl$.	$Cl_2 \cdot SO_2NH_2$.	Cl_3.
From No. 3 acid ..	122—123°	225—226°	83—84°*
From Clève's 1 : 2 : 2' $NO_2 \cdot Cl \cdot SO_2Cl$ ..	124°	227°	75·5°†
From Clève's 1 : 2 : 1' $NO_2 \cdot Cl \cdot SO_2Cl$ ..	138°	221° or 226°	83°*

A repetition of the author's work with the No. 3 acid on a large scale shows that, when pure, 1 : 2 : 2'-trichloronaphthalene has two melting-points, 88° and 84°. The higher melting-point is observed when the substance is first fused; but if it be allowed to solidify and then remelted, the melting-point is found to be 84°, and usually does not vary from this until a crystal of the original substance is added to the fused mass between 60° and 80°.

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* From $Cl_2 \cdot SO_2Cl$ by distillation with PCl_5.

† From $NO_2 \cdot Cl \cdot SO_2Cl$ by distillation with PCl_5.

On repeating Clève's investigation of the 1 : 2 : 2'-nitrochloronaphthalenesulphonic chloride, it is found that not only does the trichloronaphthalene obtained from this substance—by converting it into the dichlorosulphonic chloride and distilling this with phosphorus pentachloride—melt at 88° and 84°, as above described, but that even Clève's own method—distillation of the nitro-derivative with phosphorus pentachloride—also leads to a like result: thus, on once crystallising from alcohol 39 grms. of the product prepared by the latter method, a first separation of no less than 28 grms. was obtained which had the double melting-point 88° and 84°, whilst, of the remainder, 5 grms. more were eventually obtained pure by fractional crystallisation, 3 grms. melting at 75—76°, and the remainder at intermediate temperatures.

In fine, the 1 : 2 : 2'-trichloronaphthalene prepared either by Clève's or the authors' method, melts at 88° or 84°, and not at 75·5°. That the two are identical is also shown by the fact that both yield similar derivatives, notably a monosulphonic acid affording a potassium salt, $C_{10}H_4Cl_3{\cdot}SO_3K+H_2O$, which crystallises in sparingly soluble flat needles, and a *chloride* which is sparingly soluble in benzene, and crystallises in small rhombs melting at 173°. That Clève is in error in regarding the trichloronaphthalene from the authors' No. 3 acid as the 1 : 2 : 1'-derivative is further shown by the fact that the monosulphonic acid prepared from this latter modification affords an anhydrous potassium salt crystallising in flat needles, and a *chloride* crystallising in prismatic needles melting at 105°.

*56. "*Studies on the Constitution of the Tri-derivatives of Naphthalene, No. 12. The Trichloronaphthalene derivable from Alén's α-Nitronaphthalene-2 : 2'-Disulphonic Chloride.*" By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

By nitrating 2 : 2'-naphthalenedisulphonic chloride, Alén obtained a nitro-derivative, from which, by distillation with phosphorus pentachloride, a componnd was formed which melted at 75·5°, and was regarded by him as a trichloronaphthalene (*Ofversigt*, 1884, 97). This compound, the [θ-]derivative, was regarded by the authors as impure 1 : 3 : 3'-trichloronaphthalene (*cf. B. A. Report*, 1891, 265), and not investigated until Clève announced its supposed identity with the product obtained from the 1 . 2 . 2'-α-nitrochloronaphthalenesulphonic chloride. A repetition of Alén's work has established the correctness of the authors' view as against that of Clève.

The 1 : 2 : 2'-α-chloro-β-naphthylaminesulphonic acid (No. 3 acid) can be converted into the *xanthate*—

$$EtO{\cdot}CS{\cdot}S{\cdot}C_{10}H_5Cl{\cdot}SO_3K+H_2O,$$

which crystallises in minute prisms, and this into the sparingly soluble *sulphide-sulphonate*,

$$[S{\cdot}C_{10}H_5Cl{\cdot}SO_3K]_2+\tfrac{1}{2}H_2O$$

—by Leuckart's method (*J. pr. Chem.*, [2], xli., 218—from which the 1 . 2 . 2'-α-chloronaphthalenedisulphonic acid is obtained by oxidation with permanganate solution (*cf. Proc. Chem. Soc.*, 1893, 166).

On hydrolysing the Alén nitrodisulphonic chloride melting at 138° with aqueous caustic potash, a *potassium* salt (containing $3H_2O$) is obtained, which by reduction with ferrous sulphate and caustic potash is converted into the very soluble salt of the amido-acid. The *acid potassium* salt ($+3H_2O$) crystallises in slender, readily soluble needles, and is convertible, by Sandmeyer's method, into an α-chloronaphthalenedisulphonic acid isomeric with that obtained from the No. 3 acid, as is evident from the Table.

	From No. 3 acid, by xanthate method.	From Alén's nitro-acid.
$Cl{\cdot}C_{10}H_5(SO_3K_2)$	$\tfrac{1}{3}H_2O$	$2H_2O$
$Cl{\cdot}C_{10}H_5(SO_2Cl)_2$	prisms, m.p. 144°	dimorphous— prisms, m.p. 114° needles, m.p. 127°
$C_{10}H_5Cl_3$	m.p. 88° and 84°	80·5°

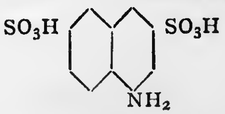
When prepared by distilling the corresponding chlorodisulphonic chloride with phosphorus pentachloride, the trichloronaphthalene from the Alén acid melts at 80·5° after once crystallising it, and even when prepared by Alén's method, *i. e.*, by distilling the nitrodisulphonic chloride with phosphorus pentachloride, melts at a higher temperature than 75·5° after it has been once crystallised: thus, 9 grms. of product from this source gave on the first crystallisation 6 grms. melting at 78—79°, from which 5 grms. melting at 80·5° were eventually obtained, whilst of the residue some melted at 75—76°, and some as low as 65—68°. That the trichloronaphthalene melting at 80·5° obtained by either method is identical with the 1 : 3 : 3'-derivative of this melting-point (*Proc. Chem. Soc.*, 1890, 129; 1891, 27) is clearly shown by the behaviour on sulphonation, as they all yield a monosulphonic acid affording a monohydrated potassium salt crystallising in long, slender needles, and a *chloride* crystallising from benzene in radiate groups of long needles melting at 154°.

*57. "*Studies on the Constitution of the Tri-derivatives of Naphthalene.* No. 13. *The α-Naphthylamine-2 : 2'-disulphonic Acid of Freund's German Patent* 27346." By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

Through the kindness of Messrs. Casella and Co., the authors were furnished with a supply of the acid sodium salt of the α-naphthylamine-2 : 2'-disulphonic acid which had been isolated from the mixed product obtained by working under the conditions of Freund's German Patent 27346. The acid sodium salt,—

$$NH_2{\cdot}C_{10}H_5(SO_3H){\cdot}SO_3Na+3H_2O,$$

crystallises in tufts in long slender needles, easily soluble in hot water. By the hydrazine method it is converted into naphthalene-2 : 2'-disulphonic acid (characterised by conversion into the chloride crystallising from benzene in prisms melting at 157°, and into 2 : 2'-dichloronaphthalene melting at 114°). On treatment by the Sandmeyer process it gave a chlorodisulphonic acid, the *chloride*, $Cl{\cdot}C_{10}H_5(SO_2Cl)_2$, of which crystallised from a mixture of benzene and petroleum spirit in two forms, being dimorphous, namely, in clusters of small prisms melting at 114°, and in needles melting at 127°. After solidifying in the melting-point tube, the chloride melted constantly at 127°, although the lower melting-point, 114°, could again be obtained by adding to the fused substance at about 100° a crystal of this form. On distillation with phosphorus pentachloride, the chloride was converted into 1 : 3 : 3'-trichloronaphthalene melting at 80·5° which was characterised in the usual way by sulphonation. These results make it evident that the constitution of the acid is identical with that of the Alén acid just described, and that both are represented by the formula—



*58. "*The Non-existence of a Trichloronaphthalene Melting at 75·5°. The Formation of Chloro-derivatives from Sulphonic Chlorides.*" By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

From the foregoing it is evident that the "trichloronaphthalene" melting at 75·5°, described by Alén, was impure 1 : 3 : 3'-trichloronaphthalene, and that of Clève impure 1 : 2 : 2'-trichloronaphthalene. The impurity was in all probability tetrachloronaphthalene, as Clève's analysis (found 46·66 per cent Cl, against 45·98 per cent), and analyses of material of similar melting-point obtained by the authors by Clève's method (found 46·52 per cent Cl) and by Alén (found 46·48 per cent Cl), give numbers too high for a trichloronaphthalene. The quantity of material obtained from each of these two sources has been insufficient to admit of more than the pure trichloronaphthalene being isolated from the sulphonation product of each. The cause of the formation of tetrachloronaphthalene is probably to be sought in the fact that when phosphorus pentachloride is used to displace the NO_2 radicle in nitro-compounds, or the OH radicle in naphthol, its action is entirely different in character from that which is exercised in the case of sulphonic chlorides. In the case of the former, substitution occurs, and higher chlorination products are almost invariably formed; in that of the latter (*cf*, "B. A. Report," 1894, 268) the halogen derivative seems to be formed by the elimination of the SO_2 of the SO_2Cl radicle, not by a displacement of the radicle by chlorine derived from the pentachloride. The presence of the pentachloride seems to assist this elimination, and to increase the yield of product, but in most cases is not necessary for the action to pursue its course; and in certain instances it is advantageous that the chloride should be heated alone. Thus, when 1 : 1'-chloronaphthalenesulphonic chloride—which is known to be remarkable for the readiness with which it gives 1 : 4 : 1'-trichloronaphthalene on distillation with phosphorus pentachloride—is heated at a temperature rising from 200°—230° during three hours so long as SO_2 is evolved, a large quantity of 1 : 1'-dichloronaphthalene (m. p. 88°) is obtained, together with small quantities of α-monochloro- and a trichloronaphthalene; 1 . 2-α-chloronaphthalenesulphonic chloride is exceptional in affording a condensation product when heated without pentachloride, hydrogen chloride befng constantly evolved, and only traces of 1 : 2-dichloronaphthalene being formed; but the other isomeric chloronaphthalenesulphonic chlorides behave, so far as examined, like the isomeric 2 : 4'-derivatives, thus—

	2 : 4' $\beta Cl \cdot SO_2Cl$ with PCl_5.	2 : 4' $\beta Cl \cdot SO_2Cl$ without PCl_5.	1 : 3' $\alpha Cl \cdot SO_2Cl$ with PCl_5.	1 : 3' $\alpha Cl \cdot SO_2Cl$. without PCl_5.
Temp. of action	190°	210—230°	195°	230—250°
Yield of 2 : 4' Cl_2	92 p. c.	62 p. c.	65 p. c.	39 p. c.

The influence of the β- as compared with the α-position of the SO_2Cl radicle on the yield by both methods is evident from these data.

It may be pointed out that not only are all doubts as to the validity of the method of determining constitution by converting sulphonic chlorides into chloro-derivatives by distillation with phosphorus pentachloride set at rest by the agreement of the results obtained with and without pentachloride, but that independent and most important confirmation of the correctness of the conclusions arrived at is afforded by the fact that the same ultimate product is obtained by directly displacing NH_2 in an amido-compound by chlorine by the Sandmeyer-Griess method and indirectly displacing it by chlorine by first preparing the xanthate, then oxidising to sulphonic acid, and distilling the chloride of this acid alone or with pentachloride. Moreover, the general agreement of the authors' results is such that they believe they are justified in regarding their conclusions as final.

*59. "*Studies on the Constitution of the Tri-derivatives of Naphthalene. No. 14. The Fourteen Isomeric Trichloronaphthalenes.*" By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

The thirteen isomeric trichloronaphthalenes considered in connection with methods leading to the elucidation of their constitution in the authors' previous papers (*cf. Proc. Chem. Soc.*, 1889—1890), have not as yet been tabulated by them with their melting-points, it being deemed desirable to set all doubts at rest before doing this. Since 1890 they have entirely revised their earlier work and extended it in order to obtain the various trichloronaphthalenes in quantities of from 35 to 50 grms.; additional methods of preparation have also been devised with the object of accumulating evidence from as many sources as possible capable of throwing light on the relative positions of any pair of radicles in the tri-derivatives. As a result, the trichloronaphthalenes have not only been characterised by conversion into monosulphonic acids, but their constitution has been determined by so many methods that there is now no room for doubt that the fourteen predicted by theory are known, and that they have the melting-points assigned to them in the accompanying table. The number of methods of preparation, each involving the determination of the relative positions of at least one pair of radicles, is given in brackets in the last column. Details regarding the properties of the trichloronaphthalenes, especially of their sulphonic derivatives, are reserved for the complete publication, as these have no bearing on the general questions considered in these notes. (See Table below).

*60. "*The Solubilities of Gases in Water under varying Pressure.*" By E. P. Perman, D.Sc.

The method used may be briefly described as follows:—A rapid current of air is aspirated through a saturated solution of the gas, the solubility of which is to be determined, and the amounts of the gas drawn off in given intervals of time, as well as the amount left in solution at the end of the experiment, are estimated, usually by a volumetric method. A curve is then drawn by plotting the amounts of gas (in grms.) in solution against the time (in minutes) during which the aspiration has been carried on. A series of tangents to this curve are then drawn; their values give the *rates* at which the gas is drawn off at different concentrations, and these *rates* are measures of the pressure of the gas in solution. The rates were then plotted against the corresponding concentrations. If the rate is proportional to the concentration, the pressure of

Trichloronaphthalenes.

State of knowledge at the end of 1888.			Constitution and melting-points assigned by					
			Armstrong and Wynne, 1889-90.		Clève, 1892-93.	Armstrong and Wynne, 1895.		
[α-]	1 : 2 : 3.	M. p. 81° (Widman)	1 : 2 : 3	81°	—	81°	[2]*
	1 : 2 : 4.	„ 92° (Clève)	1 : 2 : 4	92°	—	92°	[1]
		—	1 : 2 : 4' (1 : 2 : 5) ..	78·5° . ..	77° ; 76	78·5°	[5]
	? : 2 : 6.	„ 91° (Forsling)	1 : 2 : 3' (1 : 2 : 6) ..	92·5° . ..	90°	92·5°	[4]
		—	1 : 2 : 2' (1 : 2 : 7) ..	83—84° ..	75·5°	88° and 84°	[3]
		—	1 : 2 : 1' (1 : 2 : 8) ..	—	83°	83·5°	[2]
[γ-]	1 : 3 : ?.	„ 103° (Widman)	1 : 3 : 4' (1 : 3 : 5) ..	103°	103°	103°	[5]
[θ-]	α : 2 : 7.	„ 75·5° (Alén)	1 : 3 : 3' (1 : 3 : 6) ..	80·5° . ..	—	80·5°	[6]
[η-]	α : 2 : 6.	„ 113° (Alén)	1 : 3 : 2' (1 : 3 : 7) ..	113°	—	113°	[7]
[β-]	1 : ? : ?	„ 90° (Atterberg) . ..	1 : 3 : 1' (1 : 3 : 8) ..	87° and 90°	—	89·5° and 85°	[2]
[δ-]	1 : 4 : 5.	„ 131° (Atterberg) . ..	1 : 4 : 4' (1 : 4 : 5) ..	131°	130°	131°	[4]
[ε-]	2 : ? : ?	„ 65° (Clève)	1 : 4 : 3' (1 : 4 : 6) ..	66° and 56°	65° and 56°	66° and 56°	[6]
[ζ-]	2 : ? : β	„ 56° (Widman)					
		—	2 : 3 : 4' (2 : 3 : 5) ..	109·5° . ..	—	109°	[2]
		—	2 : 3 : 3' (2 : 3 : 6) ..	91°	—	91°	[4]

* Number of methods, each involving a determination of the relative positions of at least one pair of radicles, by which the compound has been prepared.

the gas is also proportional to the concentration, and the law of Henry holds good for the gas in question.

The aspiration was carried on in a series of five wash-bottles; the first to contain water, which makes up for loss by evaporation of the solution in the second; the second to contain the solution of the gas; the other three to contain water or some solution to absorb the gas drawn off. Air was drawn through the series of flasks by means of a water air-pump, and a regulator was placed between the pump and the flasks.

Experiments were made with solutions of ammonia, chlorine, bromine, carbon dioxide, hydrochloric acid gas, sulphuretted hydrogen, and sulphur dioxide. Henry's law was found to hold good for chlorine, bromine, carbon dioxide, and sulphuretted hydrogen, while ammonia, hydrochloric acid gas, and sulphur dioxide showed large deviations which appear to be caused by the formation of compounds of these gases with water.

Discussion.

In reply to questions from the President and Professor Armstrong as to whether the air drawn through the solution of the gas becomes saturated, Dr. Perman stated that the air does not take up as much gas as it would if the current were extremely slow, and is therefore probably not saturated in this sense. He considered, however, that this fact does not invalidate the method. The amount of gas taken up by the air in a small interval of time will be proportional to the pressure of the gas in solution, just as the amount of aqueous vapour given up by a pan of water placed in a steady current of air would be proportional to the vapour-pressure of the water. The only necessary assumption is that the gases are "perfect," as they may certainly be taken to be for the purposes of the experiment.

*61. *The Existence of Hydrates and of Double-compounds in Solution.*" Part I. By E. P. Perman, D.Sc.

The effect upon the pressure of ammonia gas in an aqueous solution produced by dissolving various salts in the gaseous solution was investigated by the method described in the preceding paper.

The gas-pressure was unaltered by dissolving 3·9 grms. sodium chloride in 50 c.c. of ammonia solution containing 4·43 grms. of ammonia.

The pressure was also unaltered when 11·23 grms. of sodium sulphate, $Na_2SO_4 \cdot 10H_2O$, were dissolved in 50 c.c. of the ammonia solution; but on dissolving 3·8 grms. of the anhydrous sulphate in the same quantity of solution, the gas pressure was increased considerably, and the increase of pressure corresponded exactly to the increase of concentration which would be caused by a loss of 4·8 grms. of water, *i.e.*, $10H_2O$ for every next drop of sodium sulphate. The author regards this as conclusive evidence that the sodium sulphate exists in solution as a definite hydrate, $Na_2SO_4 \cdot 10H_2O$.

Silver chloride at once reduced the pressure of the ammonia when introduced into the solution, thus showing that some compound of silver chloride and ammonia was formed.

In a solution containing 4 grms. of ammonia, and saturated with silver chloride, the pressure was the same as in an ammonia solution containing 2·8 grms. of ammonia in the same bulk (50 c.c.); 1·2 grms. had therefore entered into combination with the silver chloride, 0·0235 grm.-molecules (from Bodländer's table of solubilities of silver chloride in ammonia solution). This corresponds to a compound $AgCl \cdot 3NH_3$. The existence of the same compound is also indicated in more dilute solutions.

62. "*Derivatives of π-Bromocamphoric Acid.*" By F. Stanley Kipping, Ph.D., D.Sc.

The syrupy acid obtained on treating π-bromocamphoric acid with alcoholic potash (*Proc. C. S.*, 1895, 148, 33) has now been obtained in a crystalline condition, and further analysis has confirmed the view that it is a hydroxycamphoric acid of the composition $C_{10}H_{16}O_5$. (Found C = 55·1, H = 7·4; theory, C = 55·5, H = 7·4 per cent).

When π-bromocamphoric acid is warmed with aqueous potash it is first converted into an acid which is very readily soluble in water, and which is probably the hydroxy-acid just mentioned; on continued treatment, however, this initial product is transformed into a more soluble well-defined acid of the composition $C_{10}H_{14}O_4$. (Found C = 60·4, H = 7·1; theory C = 60·6, H = 7·1 per cent). This compound separates from water and dilute alcohol in large fern-like forms which seem to contain water of crystallisation, but it is deposited from a mixture of chloroform and benzene in transparent anhydrous crystals melting at about 165°; apparently it is a saturated compound as its solution in sodium carbonate does not decolourise potassium permanganate at ordinary temperatures.

An isomeride of this acid is formed in small quantities, together with other products, when π-bromocamphoric acid is heated with quinoline under suitable conditions. (Found C = 60·5, H = 7·1; theory C = 60·6, H = 7·1 per cent); this compound crystallises from water and dilute alcohol, in which it is rather sparingly soluble, in beautiful stellate forms and in six-sided plates, and melts at about 226°; it sublimes unchanged, does not give an anhydride when warmed for some time with acetic chloride, and its solution in sodium carbonate does not decolourise potassium permanganate even on boiling for a short time; these properties seem to show that it is a saturated lactonic acid.

The acid melting at about 165° is readily oxidised by warm very dilute nitric acid, the final product being a crystalline acid, which seems to have the composition $C_{10}H_{14}O_6$. (Found C = 52·0, H = 6·1; theory C = 52·2, H = 6·1 per cent); this substance is very readily soluble in water from which it is deposited in six-sided plates which seem to contain water of crystallisation; it crystallises from ethereal chloroform in lustrous prisms, melting at about 195°. When heated with acetic chloride for a short time, this acid is converted into a substance which crystallises in beautiful six-sided prisms, melting at about 250°; this product dissolves in sodium carbonate with effervescence and is probably an anhydride acid of the composition $C_{10}H_{12}O_5$, but an analysis has not yet been made.

The results indicated above afford additional facts on which to base a constitutional formula for camphoric acid, but their theoretical import cannot be discussed here.

63. "*Paraheptyltoluene and its Derivatives.*" By F. Stanley Kipping, Ph.D., D.Sc., and O. F. Russell.

This paper contains an account of *p*-heptyltoluene, $C_6H_{13} \cdot CO \cdot C_6H_4Me$, and of various other compounds which have been referred to in previous notes (Kipping, *Proc. Chem. Soc.*, 1893-94, 128, 208; and 136, 60.

64. "*Note on the Formation of a Phosphate of Platinum.*" By Robert E. Barnett.

On subliming commercial phosphorus pentoxide over red-hot spongy platinum in a current of oxygen, part of the platinum is converted into a yellow substance, which being insoluble in aqua regia can thus be separated from the excess of the metal.

The analysis agrees with the formula PtP_2O_7. It is a greenish yellow powder of rel. dens. 4·856, and is stable at a red heat unless reducing gases are present. It is insoluble in water, acids, and aqueous alkalis, but is decomposed by fusion with potassium sodium carbonate. Aqueous hydrogen sulphide slowly decomposes the compound; the exact nature of the products is still being investigated.

Saturated Ammonium Orthophosphate.—K. Kraut.—P. Schottländer is not the first chemist who has analysed this salt. Its composition is—Ammonia 25·22, phosphoric acid 34·97, and water 39·91.—*Zeit. Anorg. Chemie*, vii., Part 6.

NOTICES OF BOOKS.

Stephens's Catechism of Practical Agriculture. New Edition, Revised and largely Re-written, by James Macdonald, F.R.S.E., Secretary of the Highland and Agricultural Society; Editor of the Fourth Edition of "The Book of the Farm," &c. Twenty-second Thousand. Edinburgh and London: W. Blackwood and Sons. 1895. Crown 8vo., pp. 85.

We do not greatly admire the catechetical form of instruction in any subject; but, reserving this point, we must own that Mr. Macdonald has produced a compact and intelligible manual.

Perhaps a few subjects might have been advantageously mentioned which the author has overlooked. Thus, as regards hay and grain, the use of the Gillwell drying-machine might have been recommended for weeping summers and autumns. The inventor has been honoured with the gold medal of the Highland and Agricultural Society. Something might have been said concerning the growth of hops, of apples and pears for cider and perry, and of small fruits for the manufacture of jams, which have now an increasing commercial importance. Several other crops might have been mentioned, which, although they do not afford scope for the investment of millions of capital and the employment of thousands of labourers, should, on the good old principle of "many a mickle makes a muckle," not be overlooked.

CORRESPONDENCE.

FLIES AND MICROBES.

To the Editor of the Chemical News.

Sir,—In your notice of the last Conversazione of the Royal Society you refer to an exhibit purposing to show that flies may be carriers of microbes, and you state that it "proves the reality of the transmission of infection, *i.e.*, of pathogenic microbia, by flies." It perhaps should be pointed out that this is no new discovery, it having been already proved in various ways by several investigators, who, moreover, actually employed pathogenic bacteria in their experiments. Thus, Celli fed flies with the sputum of phthisical patients, and also with pure cultivations of typhoid, anthrax, and other bacilli, and was able to subsequently demonstrate the presence of these organisms in the excreta of these flies. Sawtschenko points out the possibility of cholera bacilli multiplying within the bodies of flies, he having found enormous numbers of these bacilli in the alimentary tract of flies after a lapse of seventy two hours from their first infection, although subsequent to that they were fed only with sterile broth, with the object, if possible, of washing out the bacilli. Moreover, Cattani and Tizzoni placed minute quantities of cholera bacilli on the bodies of flies, and found that after keeping them for an hour and a half and longer, when introduced into sterile culture media these flies gave rise to typical growths.

It may be of interest to the exhibitor, and possibly save him unnecessary trouble, if he will refer back to *Nature* of March 23, 1893, where he will find an article on flies and disease germs.—I am, &c.,

X. Y. Z.

TEST FOR MORPHINE IN UREA.

To the Editor of the Chemical News.

Sir,—In your "Notes and Queries" in the Chemical News (vol. lxxi., p. 246), I noticed that A. R. P. enquires for the best source of obtaining information as to the most delicate tests for morphine in urea.

I suppose by this he means that he has a mixture of morphine and urea. I should suggest his trying the following tests:—

1. By the ammonium sulpho-selenite test, prepared by dissolving 1 part of ammonium sulpho-selenite in 20 parts of concentrated sulphuric acid, which I expect will give him a greenish blue, changing through violet to red colour.

2. Add a little acetic acid until just acid, neutralise, and add neutral Fe_2Cl_6, the morphine blue colour is formed; if Fe_2Cl_6 is in excess, a green tint is observed; on warming the blue colour disappears and a blood-red is produced, showing the presence of an acetate. In very dilute solution Fe_2Cl_6 fixes no colouration, but is reduced to ferrous salt, and the solution will give Turnbull's blue; on the subsequent addition of potassium ferricyanide 1 part of morphine in 100 parts of water can be detected.

Perhaps it would be advisable to do some blank experiments with the above tests, and he might also look up some German translations on organic analysis at some of the scientific libraries, such as the Patent Office and the Chemical Society library.—I am, &c.,

P. L. Aslanoglou.

VOLUMETRIC DETERMINATION OF SUGAR BY AMMONIO-CUPRIC SOLUTION.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lxxi., p. 235) appears a paper by M. Zdenek Peske, in which the ordinary Pavy method is modified by using a layer of "pure paraffin oil" to exclude the air during the operation.

I am happy to bear testimony to the efficacy and convenience of this proposal, and am the better able to do so that I happen to be the originator of it. I described exactly the same method at a meeting of the Society of Public Analysts held in June, 1894; and details of the process were published in *The Analyst* for August, 1894, p. 181, *The Lancet* for July 28, 1894, p. 213, and the *Pharmaceutical Journal* for the same date, p. 90.

M. Peske's paper was read in abstract before the Chemical Society on March 21, 1895, by Professor Brauner, with whom, I believe, M. Peske had been working. Immediately the first accounts of it appeared, I informed the Secretaries of the Society that I had anticipated M. Peske, and received in return a promise that the fact should be communicated to Professor Brauner. Evidently postal communication on the Continent is very slow and uncertain, but English work is assiduously read and English ideas appropriated. The natural supposition would be that M. Peske had hit on the same idea, independently, but subsequently to me, were it not that in the abstract of his paper published in No. 150 of the *Proceedings of the Chemical Society* he makes reference to my "rather lengthy modification" of Fehling's method. As this can only refer to a modification of Fehling's test which was published in the journals above quoted as part of the same communication which suggested the use of mineral oil for excluding the air during Pavy titrations, it is difficult to resist the conclusion that M. Peske was aware of my prior employment of the plan. I am far from thin-skinned in such matters, but the present annexation is one which I cannot allow to pass without protest.—I am, &c.,

Alfred H. Allen.

67, Surrey Street, Sheffield,
May 18, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 18, May 6, 1895.

Researches on the Earths of Cerite.—P. Schützenberger.—Will be inserted in full.

Action of Fluorine upon Argon.—Henri Moissan.—Will be inserted in full.

On Fluted Spectra.—Arthur Schuster.—This does not admit of useful abridgment.

Researches on Mercurous Sulphate, Nitrate, and Acetate.—Raoul Varet.—Thermo-chemical determinations not suitable for abstraction and not of sufficient importance for insertion in full.

Presence of Chitine in the Cellular Tissue of Mushrooms.—Eugene Gilson.—The author has obtained pure chitine from *Agaricus campestris*, and has also shown its presence in ten other species of mushroom. (This, we may add, is another proximate principle common to the animal and the vegetable kingdoms).

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 112.

On a MS. of Gonperille entitled "The Art of Dyeing Cotton."—Jules Garçon.—The disinterment of a MS. work by F. D. Gonperille, published in 1807. In this bulky work the author made known the use of *chayaver*, a plant with which the dyers of India produced reds.

Programme of Prizes to be Awarded.—In 1896 the grand gold medal will be awarded for the greatest improvement in the mechanical arts; in 1897 for the greatest advance in the chemical arts; in 1899 in agriculture.

The Argenteuil prize of 12,000 francs will be awarded in 1898 for the invention most useful in perfecting French industry.

The Society's great prize of 12,000 francs will be awarded in 1895 for the discovery most useful to French industry.

The Henri Giffard prize of 6000 francs will be awarded in 1896 for signal services to French industry.

The prize of 1000 francs for workmen in manufactories of chemical products is awarded yearly.

The Melson's prize of 500 francs will be awarded in 1896, for an application of physics or chemistry to electricity, ballistics, or hygiene.

A prize of 1000 francs will be awarded in 1896 for the utilisation of a waste product.

A prize of 2000 francs will be awarded in 1896 for a new process for the production of fuming sulphuric acid or sulphuric anhydride.

A prize of 2000 francs will be awarded in 1896 for a new improvement in the production of chlorine.

A prize of 1000 francs will be awarded in 1896 for a new alloy useful in the arts.

A prize of 1000 francs will be awarded in 1896 for a substitute for sulphuric acid in dyeing, especially on silks.

A prize of 2000 francs will be awarded in 1896 for the discovery of procedures capable of yielding useful organic products.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "Japanese Art Industries," by Ernest Hart, D.C.L.
TUESDAY, 28th.—Royal Institution, 3. "Thirty Years' Progress in Biological Science," by Prof. E. Ray Lankester, F.R.S.
— Society of Arts, 8. "The Decoration of St. Paul's," by Prof. W. B. Richmond, A.R.A.
— Medical and Chirurgical, 8.30.
— Institute of Civil Engineers, 8. (Anniversary).
— Photographic, 8.
WEDNESDAY, 29th.—British Astronomical Association, 5.
THURSDAY, 30th.—Royal, 4 30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Instruments and Methods of Spectroscopic Astronomy," by William Huggins, D.C.L., F.R.S.
FRIDAY, 31st.—Royal Institution, 9. "The Radiant Heat from the Moon during the Progress of an Eclipse," by The Earl of Rosse.
SATURDAY, June 1st.—Royal Institution, 3. "Elizabethan Literature," by Prof. Edward Dowden, D.C.L.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1853.

ON ARGON AND HELIUM.*

I have examined the gas which is found enclosed in meteoric iron. The meteorite which I used was from Augusta County, Virginia, U.S.A., and had been examined by Prof. Mallet. The analysis has been published in the *American Journal of Science*, July, 1871; it contains—

Fe	88·4
Ni	10·2
Co	0·4
P	0·3
C	0·2

besides traces of Cu, Sn, Mn, Cl, S, and SiO_2. We have obtained 45 c.c. of a gas, some per cents of which disappeared on detonation with oxygen. The residue being submitted to electric sparks in presence of caustic soda underwent a slight contraction. The residue was dried with caustic soda, and I found, by means of the spectroscope, that it consists of argon, of which it shows all the characteristic marks.

We may also observe the yellow line of helium, and on comparing it with a sample of pure helium, the identity was certain. It does not coincide with the D lines of sodium.

It is interesting to find the presence of argon in a substance foreign to the earth, though it has not been recognised in the sun.

It must be remarked in conclusion that there are no lines except those of argon and helium.

I am still occupied with helium; its density is 3·88, and the ratio of the specific heats is 1·66, as with argon.

It is remarkable that the difference between the densities of argon and helium is 16, which is the case for the members of the first group and those of the second.

Helium is found in most of the minerals of the rare earths which I have examined. It is very curious that it has not been recognised earlier.—*Comptes Rendus*, cxx., p. 1049, May 13, 1895.

ON ARGON.

By HERMANN SCHILD.

Berthelot and Mendeleeff in the endeavour to locate argon in the periodic system have each given the opinion that argon is a tri-atomic modification of nitrogen, just as ozone is a modification of oxygen.

As I am not in the position to institute experiments which might promote the decision of this question, I should be happy if the following remarks could be taken into consideration in the further investigation on the nature of argon. I refer here to a treatise ("Stahl und Eisen," 1888, No. 1) which I have published in concert with Prof. B. Kirsch.

The several theorems in that essay touching on the allotropic modifications of the elements have the following contents:—An allotropic modification of an element cannot, as such, enter into a chemical combination, but can only form a molecular allocation, because, in a chemical compound, an element only comes into view as an atom and an allotropic modification exists only as a polyatomic molecule. If an element exists in the form of a modification it must, on entering into a chemical combination, be resolved into atoms and be only then combined. What can be perceived from the formulæ given by Schönbein—the first who assumed the chemical combination of a modification of an element—cannot be brought into harmony with the understanding that the modification of elements to a molecule arise by the combination of atoms of one and the same elements in different numbers.

After this reference I must remind the reader that Ramsay has liberated argon from clèveite by means of sulphuric acid, and that Berthelot has succeeded in bringing argon into chemical combination with benzene; lastly, azoimide (N_3H) is known.

If argon is triatomic nitrogen, it is only in molecular apposition and not in chemical combination, since chemically combined nitrogen has not hitherto been liberated as argon, but, on the contrary, the nitrogen obtained chemically has always, in opposition to atmospheric nitrogen, proved free from argon. Further, in the elementary analysis of Berthelot's compound of argon and benzene or its decomposition-products (if, as it can scarcely be supposed, we are not concerned with a mere molecular apposition) the argon would be set free as nitrogen, just as we cannot obtain argon from N_3H. The elementary analysis of Berthelot's compound leads us to anticipate the most weighty revelations. The production of argon from nitrogen still requires verification.

Passing to another subject, I venture to remark that the memoir above mentioned is mainly engaged with the existence of iron carbide. As it has lately been found practicable to produce the carbides of various metals, it would be a boon to science if, by producing iron carbide by Moissan's method, a contribution could be furnished to decisions on iron and steel according to their percentage of carbon.—*Chemiker Zeitung*, 1895, No. 37.

THERMOMETRIC ANALYSIS.

We are indebted to the courtesy of Mr. J. Barker Smith, L.R.C.P., for notes of his "Thermometric Method for the Estimation of Urea." He writes:—

In some articles on rheumatism published in *Medical Reprints*, 1890, July, August, and September, I showed how urea could be easily estimated in urine by placing 1 c.c. of urine in a pipette with 5 c.c. of a *good sample* of solution of chlorinated soda of the present Pharmacopœia, and, after the reaction, noting the quantity of the mixture expelled. In solving the fallacy of temperature I have discovered a still simpler method of estimating urea in urine, a method which is also applicable to the albumenoids of foods. My method is completed if necessary in the short space of three minutes, and is especially useful for the bedside in fever cases, also in the wards of the hospital, and as a control test in the physiological laboratory.

The general practitioner will find the test the simplest and most rapid of any of the tests for the quantitative estimation of urea. An ordinary cylindrical phial is found and fitted with a soft cork, a long half-ounce phial answers admirably. Measure 5 c.c. of water into the phial, and file a mark on the phial at the level of 5 c.c., add another c.c. of water and file another mark immediately over the first. No further measure is required. We pour solution of chlorinated soda up to the first mark, and then place the stem of a small thermometer into the phial, and after one minute note the temperature, *e.g.*, 56° F.; we then remove the thermometer and pour in urine to the second mark (1 c.c.), replace the cork, and holding the phial by the rim we shake vigorously for ten *seconds*, remove the cork and replace the thermometer; after about thirty *seconds* the temperature is read off which is in ratio to the urea. Suppose the temperature after the reaction is 64° F., then the difference between

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[*] Extract of a letter from Prof. Ramsay to M. Berthelot.

the first and second temperature is *eight* degrees, and this number multiplied by the factor 0·2 gives the percentage of urea, in this case 1·6 per cent (8 × 0·2). Of course, each bottle can be tested with a definite solution of urea by those who do not accept the data of a 2 per cent solution giving 10° of heat.

A suitable thermometer is brought out by Messrs. Maw, Son, and Thompson, called my "Biological Thermometer," similar to a clinical thermometer, with an extended scale and without an indicator. However, I have just found that a small foreign thermometer, with inside index, is sent out by Dollond, Ludgate Hill, for the small sum of eighteenpence, and I find it answers very well for urea estimations by my new method.

The author further states that we may estimate albumenoids in solution exactly in the same manner as we estimate urea, *i.e.*, with a good specimen of solution of chloride of soda (sodium hypochlorite) as described in the *Provincial Medical Journal* for November.

The factor to multiply the degrees of heat by, to obtain the percentage of albumenoids, is just three times greater than that used in the estimation of urea. The factor for urea is 0·2, and the factor for albumenoids is 0·6; the process is the same as for urea. 5 c.c. of the chlorinated soda solution are placed in the half-ounce phial, 1 c.c. of milk, &c., as for the estimation of urea.

Suppose the milk gives 6° of heat, as indicated by my "Biological Thermometer," then we say it contains 3·6 per cent of albumenoids (6 × 0·6). We shall not be able to estimate very weak solutions of albumens, not much weaker than ½ per cent; at the same time we can see that traces of albumen in urine do not affect the estimation of urea.

Suppose we have a substance like flour or bread. Weigh 1 grm. of bread and put it into a small mortar; add 4 c.c. of water and rub it into a paste; now add 3 or 4 c.c. of liquor potassæ, and rub into a jelly; add water to 10 or 20 c.c.; finally, estimate as for urea—*e.g.*, *percentages*.

Examples.	Biol. therm. percentage.	Actual percentage.
Serum albumen	0·9	0·88
Peptone	3·15	3·2
Fibrine	0·9	0·8
Gluten	0·72	0·78
"	1·35	1·33

The values in the second column are found by oxidimetry (*vide* "Milk," p. 8; or *Invention*, from October, 1893, to July, 1894).

Dr. Barker Smith, in a communication to the *Provincial Medical Journal*, extends this thermometric method to the estimation of alcohol in spirituous liquor. He mixes a known volume of water with an equal volume of the spirit in question, both at the same temperature. He ascertained the temperature before and immediately after mixing, when the heat read off is a measure of the percentage of alcohol.

If, *e.g.*, 5 c.c. of water mixed with 5 c.c. of spirit give 10½° of heat, the spirit is a rectified or methylated spirit. If the heat is 7½° we conclude that the spirit or tincture is of proof strength. Dr. Barker Smith admits that "we shall not be able to value the alcoholic mixtures accurately, not much nearer perhaps than 5 per cent of alcohol by measure." The author proposes extending his method to the estimation of uric acid and the urates.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on May 6th, Sir James Crichton-Browne presiding. The following were elected Members:—Mr. Henry Irving, Mr. Henry Perigal, Mrs. Slingsby Tanner, Mr. Ernest H. Fry, Mr. Thomas Muir, Mr. Harold Smith, and Mr. W. S. Smith. The special thanks of the Members were returned to Mr. George Matthey for his donation of £50 to the fund for the promotion of experimental research at low temperatures.

RESEARCHES ON THE EARTH OF CERITE

By P. SCHUTZENBERGER.

In a previous communication upon cerium I had the honour of calling the attention of the Academy to the differences presented by the successive and fractionated crystallisations of cerium sulphate obtained by the method of Debray, concerning the weight of oxide, (CeO_2), which remains as a residue on igniting these sulphates to redness.

The first and most abundant crystallisations, purified by several re-crystallisations, always re-dissolving the first deposits, yield a product the composition of which is constant.

From this sulphate—which, for the sake of convenience, we will designate as sulphate of Ce No. 1, or of Ce_1—we obtain the following results, according to the manner of analysis:—

1. Ignition to cherry redness, considering the residue as binoxide.
   Atomic weight .. .. .. $Ce_1 = 139{\cdot}5$
2. Ignition of the sulphate to white redness, considering the residue as binoxide.
   Atomic weight .. .. .. $Ce_1 = 139{\cdot}0$
   138·8
3. Determination of the sulphuric acid by barium chloride, the determination being made with the precautions indicated in my former memoir.
   Atomic weight .. .. .. $Ce_1 = 139{\cdot}5$ grms.
4. Synthesis of the sulphate, taking as the point of departure the pure binoxide of a canary-yellow colour, in a state of very fine division, obtained by burning the oxalate in the air at various temperatures.
   Dull redness .. .. $Ce_1 = 142$—143
   Cherry redness .. .. $Ce_1 = 139{\cdot}7$
   White redness .. .. $Ce_1 = 139$ to $138{\cdot}8$

If, on the contrary, we take the crystals of sulphate obtained from the last mother-liquors on precipitation with alcohol, washing in alcohol, drying and dehydration, re-solution and re-crystallisation, the results are clearly distinct, and seem to show the presence of alien earths.

In order to elucidate this question I have made a thorough study of the methods of determining the atomic weight of cerium founded on the analysis or the synthesis of the sulphate.

As an instance we have the analysis of a sulphate from these last mother-liquors, which I shall provisionally name cerium sulphate No 2, or Ce_2.

In appearance it exactly resembles cerium sulphate No. 1.

We had previously applied all the operations capable of removing the yttrium bases, the alkalies, the alkaline earths, didymium, and lanthanum.

This sulphate forms with potassium sulphate a double salt, totally insoluble in a saturated solution of potassium sulphate; the mother-liquor of the double sulphate does not show any trace of earthy oxides.

1. Analysis by determining the sulphuric acid by means of barium chloride.
   Atomic weight deduced .. $Ce_2 = 138{\cdot}75$
2. Crystallisation water of the sulphate deposited at 75° in the form of colourless prisms, isomorphous with cerium sulphate No. 1.
   Per cent .. .. 13·66
3. Analysis of the anhydrous sulphate (dried at 44° in a bath of the vapour of sulphur) by calcination to bright redness, almost white.
   a. Anhydrous sulphate used .. .. 2·120
   Oxide obtained of a decided rose-colour 1·272
   Atomic weight calculated, on supposing the oxide to be binoxide .. .. .. $Ce_2 = 136{\cdot}0$

b. Anhydrous sulphate used .. .. .. 1·8593
Reddish oxide obtained.. .. .. 1·1180
Atomic weight found, calculating the oxide as binoxide .. .. $Ce_2 = 135·7$

4. Synthesis of the sulphate by means of a finely-divided oxide, of a yellowish-rose colour, obtained on burning the oxide in air at dull redness.
Oxide used.. .. .. 1·1756
Anhydrous sulphate obtained.. 1·9262
Oxide not acted on deducted .. 0·6055

Atomic weight on calculating the oxide as binoxide—

$$Ce_2 = 142·5.$$

The comparison of these results with those of cerium sulphate No. 1 shows that—

1. The atomic weight of Ce_1, deduced from the determination of the sulphuric acid, is greater by about 1 unit than that of Ce_2 obtained in the same manner.
$Ce_1 = 139·45$. $Ce_2 = 138·75$.
2. The atomic weights of Ce_1 and Ce_2, determined by synthesis of the sulphates from oxides obtained on igniting the oxalates at dull redness in contact with air, differ but little.
$Ce_1 = 143·3$, $Ce_2 = 142·5$,
and are both higher than the atomic weights obtained by determining SO_4.
3. The atomic weights deduced on igniting the sulphates at a bright red, almost white heat, calculating the residues as binoxides, are very distinct.
$Ce_1 = 139$. $Ce_2 = 136$ to $135·7$.

For cerium No. 1 this last method gives a result very close upon the typical analysis founded on the determination of SO_4 by Cl_2Ba. The cerium binoxide from Ce_1 only undergoes a very slight loss of oxygen at white redness. On the contrary, for Ce_2 the discrepancy is considerable, for we have 138·75 on the one hand and 135·7 on the other.

Hence the bioxide of Ce_2, the existence of which is established by the results furnished by the synthesis of the sulphate from the oxide of the oxalate, undergoes, by ignition at bright redness bordering upon whiteness, a sensible loss of oxygen, and is partially reduced to the state of a sesquioxide.

4. The residue from the ignition of the two sulphates at white redness present very different colours; for Ce_1 it is nearly white, and for Ce_2 it is a light rosy-brown.
5. The sulphates of Ce_1 and of Ce_2 are isomorphous, and contain the same quantity of water of crystallisation.

It is infinitely probable that the sulphate Ce_2 analysed above is merely a mixture of the ordinary cerium sulphate No. 1 with some other sulphate.

The residual oxide from the ignition at whiteness of the sulphate Ce_2 might have as its formula $(Ce_2O_4)_2Ce_2O_3$, taking for Ce the value 138·75 deduced from the determination of the sulphuric acid. The following facts corroborate this view:—

Hitherto we have operated only on the crystals deposited in heat (75°) during the evaporation of the crude sulphates obtained by the classical treatment of cerite (see the former memoir).

The quantity of product obtained in this manner is very slight, and does not allow of the fractionation being carried further.

The treatment of the last mother-liquors has enabled me to arrive at a product which we may call Ce_3.

The analysis of the sulphate, after a prolonged purification, has given the following results:—

1. By the synthesis of the sulphate from the oxide yielded on igniting the oxalate at dull redness, the oxide being taken as binoxide,—
$Ce_3 = 142·4$.
2. By determining the sulphuric acid with $BaCl_2$,—
$Ce_3 = 137·1$.
3. By igniting the sulphate at a redness bordering upon whiteness,—
$Ce_3 = 128$ to 130.

These last results lead me to ascribe to this oxide, which is of a brownish-red, the formula—

$$(Ce^{2}_{3}O_4).(Ce^{2}_{5}O_3), \text{ or } C^{4}_{3}O_7.$$

This oxide when ignited is attacked by concentrated sulphuric acid only with great difficulty. To convert it into sulphate, the sulphates formed must be several times re-ignited after solution in water.

Hitherto I have not found it practicable to resolve the sulphate of Ce_3 into products of a distinct composition by fractionated crystallisations. It may be that we are here in the presence of a definite product.

It is still also possible that the sulphate of Ce_3 represents a double sulphate of Ce_1, yielding on ignition $Ce^{2}_{1}O_4$, and another sulphate of Ce giving on ignition $Ce^{2}_{4}O_3$. On this hypothesis we may calculate approximately the atomic weight of Ce_4. It would be equal to 134.

$$\frac{134 + 140}{2} = 137.$$

However this may be, these experiments show that cerium oxide is in cerite accompanied by small quantities of another earth of lower atomic weight, 137 or 134, capable, like cerium oxide (Ce_2O_3), of conversion into a binoxide, the sulphate of which, isomorphous with that of cerium, forms, like the latter with the alkaline sulphates, insoluble double sulphates, and the binoxide of which after ignition presents a reddish-brown colour, even without the intervention of didymium.—*Comptes Rendus*, cxx., p. 962.

ON THE COMPOSITION OF CERTAIN SOILS OF SOUTH INDIA.

By CECIL MASSEY.

As the systematic investigation of soils of various parts of the world can hardly be over-estimated, it is a pleasure for me to give the composition of a number of soils from Coorg, South India. The samples for each analysis were prepared by the most careful methods, being thoroughly mixed, and finally made to pass through a sieve of 30 meshes to the linear inch. The following results were obtained from these soils, which were collected from four different fields of arable land:—

	No. I.	No. II.	No. III.	No. IV.
Moisture	6·676	6·216	7·020	7·423
*Organic matter and combined water	3·701	4·303	3·968	4·835
Ferric oxide	4·204	3·821	4·999	3·320
Alumina	5·395	6·222	6·186	6·831
Lime	0·863	0·993	0·824	0·999
Magnesia	0·210	0·300	0·255	0·352
Potash (K_2O)	0·623	0·734	0·582	0·682
Soda (Na_2O)	0·375	0·335	0·300	0·410
Phosphoric acid (P_2O_5)	0·396	0·569	0·713	0·812
Sulphuric acid (SO_3) ..	0·120	0·207	0·186	0·200
Carbonic acid (CO_2) ..	0·211	0·302	0·190	0·235
Chlorine	0·024	0·030	0·094	0·076
Silica and insol. matter	77·202	75·968	74·683	73·825
	100·000	100·000	100·000	100·000
* Nitrogen, per cent..	0·691	0·832	0·79	0·857
Specific gravity ..	2·503	2·56	2·46	2·392

As these soils came from India it was thought advisable to examine them for microbes. It may be mentioned, *en* *passant*, that the soil of all cultivated land is teeming with microbes, whose principal function is to aid in supplying plants with their necessary food. But the exact nature of the work performed by the majority of soil microbes is still unknown. The four Indian soils (after several weeks' desiccation in transit) gave the following numbers of microbes:—

No. I.	196,000	per grm. of soil.
No. II...	253,000	,, ,,
No. III.	210,000	,, ,,
No. IV.	264,000	,, ,,

No new species were found in the samples. The nitrous and nitric microbes of Frankland, Warington, and Winogradsky were present.

In conclusion, it may be stated that the fields from which the samples were taken are for the growth of coffee.

ON A NEW METHOD FOR THE SEPARATION OF COPPER AND CADMIUM IN QUALITATIVE ANALYSIS.

By ALLERTON S. CUSHMAN.

The successful separation of small quantities of cadmium from copper has been one of the difficult operations of qualitative analysis. The method depending upon the solubility of copper sulphide in potassium cyanide is not considered by most chemists so desirable as the method of boiling the mixed sulphides in dilute sulphuric acid, on account both of its inferior delicacy and of the unpleasant character of the reagent. The last edition of Crookes's "Select Methods in Chemical Analysis" has to say on this subject:—"Cadmium sulphide dissolves with the greatest facility in boiling dilute sulphuric acid, which has no action on copper sulphide. On precipitating, by sulphuretted hydrogen, a solution containing not more than 1 m.grm. of cadmium mixed with 1000 m.grms. of copper, and boiling the black precipitate for a few seconds with dilute sulphuric acid (1 part concentrated acid and 5 parts of water), a colourless filtrate is obtained in which an aqueous solution of sulphuretted hydrogen produces an unmistakeable precipitate of yellow cadmium sulphide. Another solution of the same composition was mixed with an excess of potassium cyanide and treated with sulphuretted hydrogen gas. A distinct yellow colouration was observed; a deposit likewise took place, but so slowly that in delicacy the former experiment appears to have a considerable advantage, especially since a solution of *pure* copper in potassium cyanide also gives rise to a yellow colouration when submitted to the action of sulphuretted hydrogen."

Undoubtedly the sulphuric-acid separation is an exceedingly delicate one, when performed under the conditions detailed in the foregoing. When, however, the amount of copper present is large, and the filtration of the mixed sulphides is prolonged, traces of copper are almost certain to find their way by oxidation into the sulphuric acid solution, in which case, on addition of hydrogen sulphide, the yellow colour of the cadmium sulphide is invariably masked by the brown tinge of the sulphide of copper. Very small quantities of cadmium dissolved in an excess of dilute sulphuric acid may very easily escape detection on further dilution and addition of hydrogen sulphide, unless extreme care, cleanliness, and rapidity in filtration have been observed. Certainly few metals oftener escape detection in elementary practice than does cadmium when present in small quantity with copper.

In the solutions that were given out for analysis to the students in this laboratory, it was noticed that when cadmium and antimony were present in the same solution the cadmium frequently failed to be precipitated by hydrogen sulphide out of acid solution, but made its appearance with the precipitates of Groups III.—IV. It seemed that the only explanation of this lay in the fact that a strong solution of sodium chloride had been added to each mixture in which antimony was put, in order to prevent the separation of basic compounds of the latter metal. In the course of an investigation bearing upon this subject, it was found that when cadmium sulphide was treated with a saturated solution of one of the alkaline chlorides in the presence of dilute hydrochloric acid, it immediately dissolved to a clear solution with evolution of hydrogen sulphide. As far as can be learned, this reaction between cadmium sulphide and solutions of the alkaline chlorides in the presence of dilute hydrochloric acid has been nowhere noted. The ability of the alkaline chlorides to form double salts with many of the metals is well known, and, according to V. Hauer, cadmium chloride unites with the alkaline chlorides, and chlorides of the alkaline earths, to form compounds of the general formulæ:—$4RCl,CdCl_2$; $2RClCdCl_2$; $RClCdCl_2$ (*Pharm. Centralb.*, 1858, 292, 787; 1856, 766). On boiling cadmium oxide and cadmium carbonate with ammonium chloride solution a double crystalline compound has been obtained with the formula $2NH_4Cl,2CdCl_2,H_2O$ (Graham Otto, "Aufl." 5, iii., 828).

In order to see if a strong neutral solution of ammonium chloride had any action on cadmium sulphide, the following experiment was made:—A solution of cadmium nitrate was precipitated by hydrogen sulphide, and the precipitate thoroughly washed by decantation with boiling water until free from last traces of sulphuretted hydrogen. The precipitate was then thrown on a filter, sucked dry, and finally dried at 100°. A quantity of this dried calcium sulphide was suspended in a concentrated solution of ammonium chloride in a flask which was connected with a Varrentrapp-Will tube containing a solution of lead acetate. The temperature of the mixture was then gradually raised without producing any precipitate in the bulb-tube until protracted boiling had taken place, when a decided precipitate of lead sulphide appeared in the tube. It is a well-known fact that solutions of ammonium chloride become acid on prolonged boiling owing to dissociation and escape of ammonia (*Ann. Chem.*, Liebig, cxxviii., 189; Graham Otto, iii., 485). As the partial reaction in this case only began after prolonged boiling, it is probable that it was due to the formation of free hydrochloric acid in the solution. On addition of dilute hydrochloric acid to the mixture in the flask, the cadmium sulphide immediately dissolved. On repeating the foregoing experiment, using sodium chloride instead of ammonium chloride, no hydrogen sulphide was given off except in the presence of free hydrochloric acid. In a general way the reaction is perhaps best expressed by the following:—$CdS+2RCl+2HCl=CdCl_2,2RCl+H_2S$.

This solubility of cadmium sulphide in acidified concentrated solutions of the alkaline chlorides renders possible an exceedingly delicate method of testing for cadmium. If to 2 c.c. of a solution containing a small amount of cadmium, 10 c.c. of a saturated solution of salt and a few drops of dilute hydrochloric acid be added, hydrogen sulphide fails to produce any precipitation even up to saturation of the liquid by the gas. If now a few drops of dilute ammonia be allowed to flow down the side of the tube a distinct yellow ring or layer of cadmium sulphide appears at the junction of the two liquids. By this method 1 c.c. of a solution containing 0·1 m.grm. of cadmium sulphate developed a distinct yellow ring in a few minutes, while 3 drops of the same solution, equal to an amount less than 0·01 m.grm. of cadmium, developed a perceptible ring on standing half an hour.

The fact that copper sulphide has been found quite insoluble in the reagents offers an easy and delicate method of separating the two metals. When the metals are present in comparatively large quantity it is only necessary to treat the mixed sulphides with an excess of a strong solution of salt and a little dilute hydrochloric acid, when, on warming, the cadmium sulphide entirely dissolves. On dilution of the filtrate and addition of hydrogen sulphide, the cadmium sulphide is re-precipitated. The method is more accurately carried out in this laboratory as follows:—About 2 c.c. of the solution containing the two metals is made slightly acid with hydrochloric acid, and about 20 c.c. of a saturated salt solution added, the solution warmed, and hydrogen sulphide passed through until the copper is all precipitated and the hydrogen sulphide is present in excess. The copper sulphide is then filtered off through a dry filter, and the filtrate run into a dry test-tube. The filtrate collected in the tube should be perfectly clear, as the slightest dilution begins to precipitate the cadmium. Therefore if a few drops of water be allowed to run down the side of the test-tube, a yellow line will be formed at the junction of the two liquids if cadmium is present. Diluted ammonia may be substituted for water with advantage if the amount of cadmium present is very small, as it developes the yellow layer more rapidly than water does. On the other hand, if traces of other metals are present through incomplete removal in the group separations, the result will be obscured by the use of ammonia.

This method has been thoroughly tested with mixtures of solutions of copper and cadmium in varying proportions, and has been found extremely sensitive. Sometimes it has been found that, when very minute quantities of copper are present, the copper sulphide is precipitated in the strong solution of sodium chloride in so finely divided a condition that it is impossible to remove it completely by filtration. In this case the addition of a few drops of a solution of copper sulphate and re-precipitation with hydrogen sulphide obviates the difficulty.

In the hands of students the method has given uniformly good results when carried out with the ordinary care necessary to the success of all analytical processes. As some other metallic sulphides, notably those of lead and bismuth, are found to be soluble in strong acidified solutions of the alkaline chlorides, these metals must be as completely removed as in any other test for cadmium.

The bearing of these reactions with lead, bismuth, and cadmium sulphides, on qualitative and quantitative separations, will be more fully studied in this laboratory in the future. The simplicity of the reagents used, and the delicacy of the test for cadmium, will probably commend the method to chemists and instructors in qualitative analysis.—*American Chemical Journal*, vol. xvii., No. 5.

ON THE ATOMIC WEIGHT OF OXYGEN.

Synthesis of Weighed Quantities of Water from Weighed Quantities of Hydrogen and Oxygen.

By EDWARD W. MORLEY.

Many most valuable contributions to our knowledge of the atomic weight of oxygen have been made within ten years by Rayleigh, by Dittmar and Henderson, and by Scott, in England, by Leduc in France, by Thomsen in Denmark, and by Cooke and Richards, by Keiser, and by Noyes in America. My own experiments began many years before I learned that others were at work on the subject; but as no assistance could be afforded me, and as, till after the completion of the experiments described in this paper, the whole expense fell upon me, the progress made was so slow that it often seemed hardly worth while to go on.

The process used by Berzelius and Dulong, and by Dumas was first studied. Perhaps the opinion unfavourable to its precision which was formed may be modified by the experience of others, but until our knowledge of the properties of cupric oxide becomes such that we can easily prepare an oxide free from everything but copper and oxygen, the process can hardly be made capable of satisfactory precision. But it cost a year to come to this decision.

It also cost much time to learn how, with ease and certainty, to prepare hydrogen of sufficient purity. When this was accomplished, the method of weighing the gas directly had to be chosen. Some of my globes had a capacity of 21·5 litres, so that 1·8 grms. of hydrogen could be weighed in one of them. Since the weight of such a globe can be determined with a mean error of less than a tenth of a m.grm. in a single weighing, the process is not an unpromising one. But while it is easy to prepare pure hydrogen, and easy to weigh it, it is by no means easy to introduce it into the globe without contamination, either by mercurial vapour, from a mercurial air-pump, or by organic vapours from the lubricant of a piston air-pump. The difficulties could be surmounted, if no alternative method were available. But there is a better method, and it is easy.

One method of directly weighing hydrogen is, to weigh a suitable gas-bottle with its drying train, then to generate hydrogen in it by the solution of a metal in an acid or in an alkali, and then weigh again. Some of the forms of apparatus which were tried would permit me to weigh over 4 grms. of hydrogen in each experiment. But it was impossible to procure easily a metal which gave pure hydrogen, or hydrogen which could be purified with a simple purifying train. Nothing would answer my purpose except zinc re distilled in a vacuum so as to free it from carbon.

There remained only the costly recourse to the method depending on the use of palladium. Chirikoff seems first to have suggested the use of palladium as a means of purifying hydrogen. I began experimenting with the present investigation in mind in 1883, though on a small scale.

The experiments to be described in this paper consist of twelve syntheses of weighed quantities of water from weighed quantities of hydrogen and of oxygen. The hydrogen was absorbed in 600 grms. of palladium; the oxygen was weighed in two globes, in the form of gas. Full details of the experiments are ready for a publication of the Smithsonian Institution, to which those are referred who care to know the nature of the apparatus used, and to see the quantities determined by the balance or the eudiometer, unmodified by any computation. The present paper is but a brief abstract of one part of that paper, giving the final results of each of the experiments, and such a general description of the apparatus as may be sufficient for many.

Apparatus for Producing and Weighing Water.

The apparatus for producing and weighing water consisted of a thin glass tube some 22 c.m. long and 25 m.m. in diameter (Fig. 1). Midway in its length were inserted two tubes, ending within in two platinum jets parallel to the axis of the tube. Just above these jets were two platinum wires for inflaming the jet of hydrogen or of oxygen. The gases came to the jets through drying tubes filled with phosphorus pentoxide, so that the uncombined gases could enter, but the water produced could not escape, if the apparatus were properly used. The ends of the drying tubes were furnished with ground joints by which they could be joined to the apparatus for regulating the admission of the gases. The volume of the apparatus was not far from 250 c.c., and the weight nearly 100 grms. Before using it, it was exhausted to the ten-thousandth of an atmosphere, and closed by fusion. Its volume was determined and it was then weighed accurately against a counterpoise of the same volume and of 35 or 40 grms. greater weight.

Apparatus for Weighing Hydrogen.

My plant for weighing hydrogen contained 600 grms. of palladium; in the first and second experiments this was divided between two tubes, but in the rest it was all in one tube. Some trifling modifications of its form were made after each accident to it; all these are mentioned in the paper to be issued by the Smithsonian Institution. In the final form no stopcock was used on this tube; but even in those experiments in which the stopcock was still attached to the tube, it was never used for any purpose except to regulate the current of gas for a moment. A most fruitful source of annoyance, or even of serious error, was avoided by depending solely on fusion for closing this tube. The tube containing palladium having been connected by fusion to the source of hydrogen shown at Fig. 1 in my paper on the "Volumetric Composition of Water" (*Am. Journ. Sci.*, xli., 225), the palladium was heated, and a current of the gas was passed for half an hour or more. The tube was then closed by fusion, the metal was cooled, and the gas was passed into it to saturation. The tube was then again opened and a current of the gas was passed for two or three hours, so as to remove any nitrogen which might conceivably have accumulated, after which it was closed by fusion at all points, its volume was determined by hydrostatic weighing, and its weight was determined by the method of reversal, using a counterpoise of the same volume and the same weight. The observations of weight were repeated at intervals.

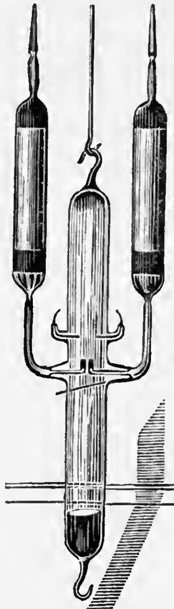

Fig. 1.

Apparatus for Weighing Oxygen.

The two globes used for weighing oxygen contained 20·0 and 21·5 litres. They were provided with counterpoises which were equal to them in volume when the globes were exhausted, and the expansion of the globes produced by filling them with gas was compensated, the compensation being a simple and accurate method of dispensing with the observations of pressure and temperature which would have been necessary in order to compute corrections for differences of volume. The globes were exhausted with a Toepler pump to one part in thirty or fifty thousand, and filled with pure and dry oxygen. They were weighed as stated before. It was thought that the amount of mercury vapour which contaminated the oxygen was negligible, experiments seeming to justify this opinion. That the oxygen was free from chlorine, although made from potassium chlorate, was proved by suitable examination of the water produced from it.

Balance.

The balance used was made by Becker, of Rotterdam, and carries a kilogrm. in each pan. It was procured for this investigation, and has been used for nothing else. It was set up in a room of nearly constant temperature, on the stone cover of a closet or cave of a little more than a metre in each internal dimension. Under the balance, fastened to the under side of this stone cover, is a reversal apparatus by means of which any one of three pairs of objects may be suspended from either pan of the balance without opening the cave or approaching the balance. With this apparatus, objects to be weighed were placed in the cave, each pair in its desiccator, and left in dry air for hours before weighing. After weighing each pair of objects at least four times, by reversal, at intervals of at least half an hour, it was hoped that the weights might be considered fairly determined. The probable errors of the results seem to justify this hope.

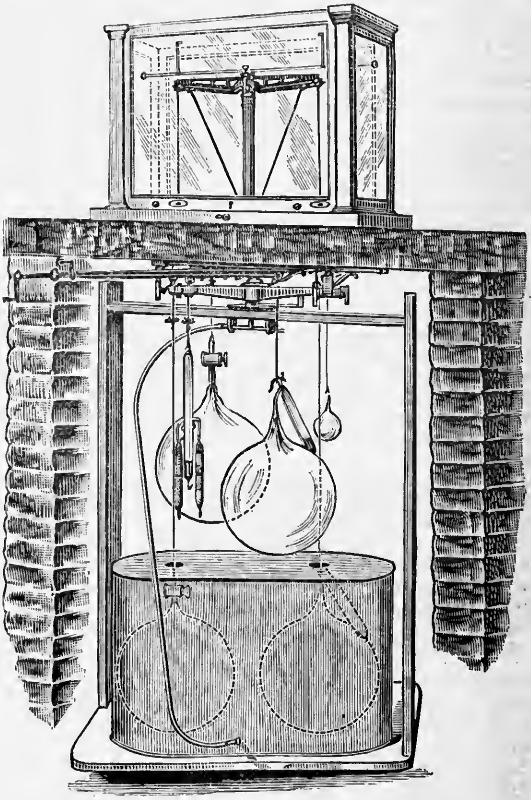

Fig. 2.

Fig. 2 shows the balance and the mechanism for weighing by reversal. The apparatus was photographed while supported temporarily for the purpose, and the drawing made from the photograph as accurately as the artist could well do it, but some details are not quite correct. Hooks attached to the pans of the balance pass down through the stone cover of the vault. Six hooks carrying the globes and other objects are supported by six arms just below the stone. By means of the handles seen well to the left, any one of these six hooks can be engaged in either of the first pair, and then left attached to it, and free from contact with the arm. The current of dry air needed to supply the desiccators was introduced through the axis of the reversal mechanism, as suggested by the rubber tube in the drawing. The desiccators for the second and third pairs of objects are not shown.

Combining the Gases to Produce Water.

When the hydrogen, the oxygen, and the apparatus for containing the water produced, had been weighed, the apparatus was set together. The apparatus for producing water was opened by breaking off the tubes near the ground-joints of the drying tubes; of course, taking means to prevent the admission of moisture with the entering air. The apparatus was then connected to the system of stopcocks and gauges for controlling the admission of the gases. To this same system were then connected the palladium tube and the two globes of oxygen. Before these were opened to admit gases to the system, the combustion apparatus and the system of tubes were exhausted by a Toepler pump which was permanently connected to the apparatus. After the pump was shut off, the gases were admitted to the connecting tubes and into the combustion apparatus itself, where they were ignited by sparks between the wires for the purpose. Immersion in water kept this part of the apparatus at a suitable temperature.

After the combustion was ended, the palladium tube and the globes for oxygen were closed, and the water which had been produced was cooled to −20°, so as to make the tension of its vapour small. The Toepler pump again exhausted the apparatus, and the gas withdrawn from the globes and the tube of palladium, but remaining unconsumed in the apparatus, was transferred to an eudiometer. The combustion apparatus was closed by fusion and weighed together with the parts removed in the manipulation of opening and closing it. The same was done with the tube containing palladium, which was also weighed hydrostatically, to detect any change of volume due to heating. When the globes had been weighed, it was known how much had been withdrawn from each source of gas. The unconsumed residue being measured and analysed, and the proper subtraction being made, it was known how much of each gas had been combined to form water, which gave the ratio sought. From the weight of water produced, compared with the weight of hydrogen used, was obtained a second determination of the ratio.

No rubber joints were used about the apparatus; all connections were made by fusion, except where parts had to have their weight preserved unchanged, when they were connected to adjoining pieces by suitable ground-joints made tight with paraffin.

The results of the twelve experiments made by this method are given in the following table.

Weights of hydrogen, of oxygen, and of water formed, with ratios deduced:—

Hydrogen.	Oxygen.	Ratio.	Water.	Ratio.
3·2645	25·9176	15·878	29·1788	17·877
3·2559	25·8531	15·881	29·1052	17·878
3·8193	30·3210	15·878	34·1389	17·873
3·8450	30·5294	15·880	Apparatus broken.	
3·8382	30·4700	15·877	34·3151	17·881
3·8523	30·5818	15·877	34·4327	17·876
3·8297	30·4013	15·877	34·2284	17·875
3·8286	30·3966	15·878	34·2261	17·879
3·8225	30·3497	15·879	34·1742	17·881
3·8220	30·3479	15·881	34·1743	17·883
3·7637	29·8865	15·881	33·6540	17·883
3·8211	30·3429	15·882	34·1559	17·878
Means ..		15·8792±0·00032		17·8785±0·00066

Besides the full details of experiments here briefly described, the paper in the hands of the Secretary of the Smithsonian Institution contains three series of determinations of the density of oxygen under normal conditions at the sea-level in latitude 45°; two series of similar determinations for hydrogen by the processes hitherto used, which are rejected for a suspected source of error incident to such determinations; three series of determinations of the density of hydrogen by a new method which avoids the error suspected, which were carried out with two independent apparatus; and a determination of the volumetric composition of water by a process which is, in one respect, similar to that lately used by Leduc. The combination of these quantities gives a third determination of the atomic weight of oxygen, of which the trustworthiness, as far as can be judged from probable errors, is equal to that of any determination hitherto made; and it agrees absurdly well with the two results from the syntheses. In this work on the densities I have had generous help from Mrs. Amasa Stone, from Messrs. Warner and Swasey, from Mr. C. W. Wason, from the East Cleveland Railroad Company, and the succeeding corporation, the Cleveland Electric Railway Company, and from the Smithsonian Institution; which I am glad of the opportunity to acknowledge.

The following table gives the more important results of the work on the densities and volumetric composition, together with the final results of the experiments described in the present paper. To it is appended a table showing the results of previous experimenters, which Professor F. W. Clarke had revised for a forthcoming work, and which he kindly furnished to me:—

Density of oxygen, latitude 45°	1·42895±0·000034
Density of hydrogen	0·08987±0·0000027
Ratio of densities	15·9002 ±0·00061
Volumetric composition of water at 0°	2·0027 ±0·00014
Atomic ratio from densities and volumetric ratio	15·879 ±0·0011*
Atomic ratio, syntheses	15·8792 ±0·00032
Molecular weight of water, syntheses	17·8785 ±0·00066

Results of other Experimenters.

	Atomic ratio.
Berzelius and Dulong	15·894 ±0·057
Dumas	15·961 ±0·007
Erdmann and Marchand	15·975 ±0·011
Cooke and Richards	15·869 ±0·0020
Keiser, 1888	15·951 ±0·0011
Rayleigh, syntheses	15·89 ±0·009
Noyes	15·897 ±0·0017
Dittmar and Henderson	15·867 ±0·0046
Leduc	15·881 ±0·013
Morley	15·879 ±0·0003

	Ratio of densities.
Regnault, corrected by Crafts	15·9105±0·0044
Rayleigh, 1888	15·884 ±0·0048
,, 1892	15·882 ±0·0023
Cooke	15·890 ±0·0067
Leduc	15·905 ±0·015
Morley	15·900 ±0·0006

Volumetric Composition of Water.

Scott	2·00285
Morley, eudiometer (reduced to 0°)	2·0008
Leduc	2·0038
,, corrected according to my reduction	2·0024

While the value 2·0002, which I obtained by direct measurement, is the value which I am certain would be obtained by others working with pure gases in an apparatus of the nature and dimensions used, it is obvious that the result is not a measurement of the quantity desired, but that it is complicated with a phenomenon which is hinted at by the fact that both my own experiments and those of Scott in an apparatus of similar dimensions, yield a result in which the volume of the oxygen comes out too large. But whether I shall have the means of elucidating the supposed cause remains for the future. I think we may safely trust the values obtained by Scott and by myself in our last determinations:—

Scott	2·00285
Morley	2·00270

—*American Chemical Journal*, xvii., No. 4.

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* Atomic ratio, from densities and volumetric ratio by Scott's experiments, 15·878.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, May 24th, 1895.

Captain W. de W. Abney, President, in the Chair.

Dr. Kuenen read a paper entitled "*On the Condensation and the Critical Phenomena of Mixtures of Ethane and Nitrous Oxide.*"

If the vapour of a pure substance is compressed at constant temperature, when a certain pressure is reached the vapour commences to condense and the pressure remains constant until all the vapour is liquefied. On taking the pressure and temperature as co-ordinates, and plotting the corresponding temperatures and pressures at which liquefaction takes place, a curve is obtained which is called the vapour-pressure curve, and this curve ends at the critical temperature and pressure of the given substance. On the other hand, if a mixture of two vapours is compressed at constant temperature, the pressure no longer remains constant while condensation is taking place, but gradually rises. The points at which condensation commences and ends lie on a U-shaped curve, having its vortex turned towards the direction of increasing temperature. Such a curve the author calls a "border-curve." The point at which a line parallel to the axis of p touches a border-curve corresponds to the critical point (R) of the given mixture. In all temperatures higher than that corresponding to R there is no condensation into liquid possible, while for any temperature below the critical temperature there are two vapour-pressures, one corresponding to the commencement and the other to the conclusion of liquefaction. The envelope of all the border-curves for mixtures containing different proportions of the two bodies is a curve, called the plaitpoint-curve, joining the critical points of the two constituents. The point of contact (P) of a border-curve with the plaitpoint-curve corresponds to the plaitpoint on van der Waal's thermodynamic surface. If when we go along the border-curve, starting from its lower branch, we first reach R, then P, and if we indicate the temperatures corresponding to P and R by T_P and T_R, then for temperatures between T_P and T_R, as the pressure is increased, the quantity of liquid first increases, reaches a maximum, and then after that decreases till it disappears. This is called retrograde condensation of the first kind, and has been observed by the author in the case of mixtures of methyl chloride and carbon dioxide. If P, however, lies beyond R, the process of condensation for temperatures between T_P and T_R is different. In this case the volume of vapour increases, reaches a maximum, and then decreases. This constitutes retrograde condensation of the second kind. It was with a view to the experimental observation of this second kind of retrograde condensation that the author undertook his observations. A series of observations were made with each of the pure gases, and gave the following values for the critical temperature:—

Ethane	32·3° C.
Nitrous oxide	36·1° C.

In the case of the mixtures the very interesting result is obtained that the critical temperature is in some cases less than that of either of the constituent gases. Thus a mixture containing 10 per cent of C_2H_6 has a critical temperature of 32°, the same critical temperature as for pure ethane. All mixtures containing more than 10 per cent of ethane have a lower critical temperature than 32°, the lowest critical temperature obtained being 25·8°, and corresponds to a mixture containing equal volumes of ethane and nitrous oxide. Another important point is that the border-curves do not all lie between the vapour-pressure curves of ethane and nitrous oxide. Hence for any temperature there is some mixture which gives a maximum vapour-pressure. It also appears, from the curves given in the paper, that the maximum vapour-pressure is obtained with almost the same mixture at all temperatures, and that this maximum vapour-pressure does not disappear with increase of temperature, but remains even up to the critical region.

For mixtures containing between 20 and 50 per cent of C_2H_6 retrograde condensation of the second kind takes place, but the author has not been able to observe it, since the difference between T_P and T_R for the two substances experimented on cannot be more than 0·1°, and the temperature could not be maintained sufficiently constant to hope to be able to detect any phenomenon taking place over such a small temperature range.

The author showed his arrangement for stirring the liquid and vapour in the experimental tube, so as to prevent any retardation of the different phases due to slow diffusion in the long narrow tubes employed. A small piece of iron, with enamel beads on the ends, is enclosed in the experimental tube; and by means of a small magnetising coil, which surrounds the jacket used to keep the temperature of the tube constant, this piece of iron can be moved up and down the tube so as to keep the liquid and vapour thoroughly stirred.

Prof. Carey Foster and Prof. Ramsay complimented the author on the very lucid way he had expounded a by no means easy subject.

Dr. Sidney Young congratulated the author on the able use he had made of his lucky discovery of two bodies such that their mixture should have a lower critical temperature than that of either of the pure substances. Prof. Ramsay and he (Dr. Young) had made experiments on the vapour-pressure of mixtures of alcohol and ether, and had found great difficulty in preventing the separation of the components when the volume was altered, and he could therefore thoroughly appreciate the utility of the author's device for overcoming this difficulty. They had also experienced considerable difficulty in filling the tube with a mixture of known composition and free from air, and he considered that when dealing with mixtures it was better to employ gases, although they could not be obtained in so perfect a state of purity as liquids, on account of the greater ease with which a mixture of known composition can be obtained. The plan of making separate observations on the pure substances was a good one, and, considering that the author measures the increase of pressure during the process of condensation, so that any air which happens to be present produces the maximum effect, the small rise in pressure obtained indicated a high degree of purity in the gases employed. He would like to ask the author if, in the case of mixtures, he found it possible to determine accurately the point where condensation commenced and ended, for with the alcohol and ether mixtures they had found it very difficult to determine these points. He also hoped the author would continue his observations in the direction indicated in the paper.

Mr. Inwards suggested that, in the case of liquids which act on iron, the iron stirrer could be enclosed in glass or india-rubber. It might also be possible to obtain more efficient stirring by means of a small fan or propeller worked by an electro-magnet rotating outside the tube.

Dr. Kuenen, in his reply, said that, when the mixtures were well stirred, the pressures at which condensation commenced and ended were well marked.

Mr. Burstall commenced the reading of a paper "*On the Measurement of a Cyclically Varying Temperature.*"

The experiments were undertaken with a view of measuring the temperature inside the cylinder of a gas-engine, at different points of the stroke of the piston. A modified form of platinum thermometer is employed to measure the temperature, and since the variations in temperature are extremely rapid, the wire had to be very thin and unprotected by any covering such as is ordinarily employed. The leads of the thermometer pass through a slate plug fixed in a seamless steel tube, asbestos being used as a packing to prevent leakage. The resistance of the thermometer was measured by means of a Wheatstone's bridge. Since the temperature of a certain part only of the *working* stroke had to be measured, the galvanometer circuit was broken in two places; one of these breaks was closed by means of a cam on the shaft of the engine at a given point of each revolution, while the other was closed when an explosion took place by means of a relay worked by the pointer of a steam-engine indicator attached to the cylinder of the engine.

The remainder of the paper was postponed till the next meeting.

NOTICES OF BOOKS.

Handbook of Stereochemistry. ("Handbuch der Stereochemie.") With the Co-operation of Dr. Paul Walden, Tutor in Physical Chemistry. Edited by Dr. C. A. Bischoff, Professor of Chemistry at the Riga Polytechnicum. With 250 Figures in the Text, and Portraits of L. Pasteur, Le Bel, and J. van 't Hoff. Vol. I. Frankfurt-on-Mayn: Published by H. Bechold. 1893.

When graphic formulæ were first brought into use it was erringly supposed, by not a few readers, that their object was to express the probable arrangement of the atoms in each compound. Setting aside other objections, it was at once manifest that the structure of solid bodies could not be conceivably represented on a plane surface. But we have now arrived at the concept of chemistry in space—the doctrine of geometrical isomerism, better known as stereo-chemistry. This important development of our science has hitherto scarcely received in Britain the attention to which it is entitled.

We certainly find the recognition of stereo-chemical principles in memoirs and lectures; but we have no work which presents a full view of the chemistry from the special point of view. Hence the work before us will merit, and doubtless receive, the careful attention of all students who are sufficiently versed in the German tongue.

Two shortcomings it certainly in our opinion displays; it has no table of contents, and the authors nowhere present a full view of their theories free from everything which may be regarded as scaffolding. The object of the book is to win, if possible, further adherents for stereochemistry. So rapid has been the recent progress of this region of chemistry that it becomes difficult for the student to combine the details, the ideas, and suggestions scattered in journals and pamphlets, into a general picture of the development and the present state of stereochemistry, the rather that every year is fruitful in results which have to be verified and co-ordinated with that which is already recognised.

The great proof of the value of stereo-chemistry is that it is daily leading to new experimental researches.

The authors give, in the first or general part of this book, a general view of the fundamental principles of stereo-chemistry and their historical development. They take up the work of Pasteur (1860), of Kekulé (1861—1864), and of Butlerow (1863).

Here our attention is called to the different senses which Kolbe and Gerhardt attach to the term "constitution." Like Kekulé, Gerhardt understands by "constitution" the true molecular arrangement of the atoms, whilst Kolbe believes that our researches will never lead us to a clear view of the manner in which the several atoms are respectively arranged.

The views of that epoch may be summarised as follows:—"The chemical behaviour of each atom contained in a compound molecule of any element is conditioned, on the one hand, by its nature and the chemical arrangement in the molecule, and on the other by the nature, quantity, and chemical arrangement of the other atoms contained in the same molecule."

In 1863 Carius introduced the concept of "physical isomerism."

The first attempt to represent chemical formulæ with regard to their special extension is due to Kekulé (1867).

William Thomson in 1867 published a treatise in which he maintained that the rings of Helmholtz were the only true atoms.

The first attempt to represent the position of the atoms in space is ascribed to Gustav Hinrichs, of the University of Iowa, in 1867. His views were made known in a lithographed MS. entitled "Chemistry as the Mechanics of the Panatoms."

In 1869 Paterno, in experimenting on the pentachlorinised ethan and dibrom-ethan, came to the conclusion that there was here a finer special isomerism.

In the same year Wislicenus, in his studies on lactic acid, recognised the insufficiency of structural formulæ.

In 1875 F. W. Clarke published his "Chemistry of Three Dimensions"; and in the foregoing year there appeared the memorable pamphlet of J. van 't Hoff, taking his stand on the theory of valences.

Le Bel writes, "I have succeeded, by combining the original principle of Pasteur with the discoveries of modern chemistry, in finding a simple means of foreseeing the rotatory power."

Space does not permit us to enter upon the recent researches of Fock, Wislicenus, Werner, Meyerhoffer, Vaubel, Armstrong, and other investigators.

In the second, or special, part of the work, the authors discuss the relation of the stereo-chemical theories to the optical rotatory power of organic bodies, geometrical isomerism, and the consideration of special relations in chemical reactions. Here much may be evidently expected, as we shall doubtless find in the next volume.

Might it not have been advantageous if the authors had applied their theories also to inorganic chemistry?

A Discussion of the Forces of Chemical Dynamics. ("Eine Discussion der Kräfte der Chemischen Dynamik.") Three Discourses by Dr. Ludwig Stettenheimer. 8vo., pp. 88. Frankfurt-on-Mayn: Bechold. 1895.

Dr. Stettenheimer opens his discussion by taking exception to the ordinary definition of chemistry as the doctrine of substances, their properties, and mutations. To such a definition he objects as being a more external characterisation, embracing not only a great part of pure physical processes, but in a certain respect returning to the question to be explained. Hence he takes another point of view, attacking the subject in a more abstract manner, and from the side of universal mechanics.

Thus, were chemistry fully constructed it would form, he holds, the counterpart of astronomy. "As astronomy treats of the applied, observing and describing mechanics of the greatest bodies known to us, so chemistry must be regarded as the corresponding mechanics of the minutest tissues." The author admits that this definition is not yet absolutely precise, since it does not exclude certain physical processes.

But we fear that he does not do justice to the following consideration: mechanics would be a conceivable Science if there were in the universe only one kind of matter. The problem, *e.g.*, of "three bodies" could be discussed and solved. But if there were only one element in existence chemical science could not exist, could not even be imagined! Is there not here a fundamental distinction independent of and totally other than the difference between the immeasurably large and the almost infinitely minute?

The author considers that for his theory the molecule no longer exists as a fundamental concept. In its place would come the "chemical system."

We are all well aware that Dr. Stettenheimer points out not a few flaws and shortcomings in the foundations of our Science. If he can remove what is questionable, and throw a new light upon what is doubtful, we shall hold him welcome.

It will perhaps be most serviceable to our readers if we quote the author's conclusion:—

"In electrolysis we have always obtained together the electric current and the chemical transposition in a homogeneous system, whence there have originated a series of theories to harmonise the two phenomena.

"As already shown it is the matter, *i.e.*, the atoms and groups, which arranges itself in a peculiar manner on the electric charge of a substance. We must therefore think either not at all, or only in the last place, of an electric fluid which passes over to the ions, perhaps coating them with a thin stratum, and which, by occasion of the transposition, effects the transfer of electricity. The ions are not thus electrically charged at the electrodes, but the current itself consists in the chemical transposition.

"Electricity does not play a jointly influential part in chemical transformation, but the ordinary chemical facts are not conceivable otherwise than as jointly eliciting such phenomena as the electrical. These are merely consequences of the chemical forces, and have their peculiarities only in peculiar arrangements of existing systems.

"Everything shows that there are no especial chemical forces distinct from mechanical forces; therefore, also, no molecular force different from the chemical force; no cohesive, adhesive, no electric force, for which the same does not hold good. Everything indicates the pure mechanical reciprocal action of matter (or matters?) characterised here, merely by the fact that they attach themselves in a certain manner to the minutest particles."

Theoretical and Practical Ammonia Refrigeration. A Work of Reference for Engineers and Others employed in the Management of Ice and Refrigeration Machinery. By **Iltyd I. Redwood**, Assoc. Member American Society of Mining Engineers; Member of Society of Chemical Industry, England. 12mo., pp. 146. New York: Spon and Chamberlain. London: E. and F. N. Spon. 1895.

Refrigeration is coming into increasing use in a variety of chemical manufactures, and, as the ammonia machine is under many circumstances the most economical and convenient, there is evidently need for the little book before us. We are sorry to find our old enemy Beaumé flourishing here in full luxuriance. Of course Twaddell, being only adapted for solutions specifically heavier than water, cannot be used for ammonia; but there can be no objection to a direct specific gravity scale, simplified by omitting the decimal point and any figure to its left hand. The explosion of a mixture of gaseous ammonia and common air is of course theoretically possible; but, after a life spent chiefly at chemical works, we must regard it as an exceptional occurrence.

The action of ammonia upon copper and its alloys is well known, and should be guarded against. But the chief danger of working with ammonia, liquid and gaseous, is the highly injurious effect upon the eyes.

The author uses the term "brine" for the watery solution of calcium and magnesium chlorides, as well as of sodium chloride. For dissolving calcium chloride the author recommends stirring or boiling. He would find it more convenient to place the lumps of the salt on a shelf covered with sacking, &c., fixed on the upper part of the bath, and thus effecting solution and filtration at one and the same time.

Mr. Redwood's recommendation to use for lubrication merely mineral oils of high viscosity is judicious, and if duly attended to will save much trouble.

CORRESPONDENCE.

ARGON IN MINERALS.

To the Editor of the Chemical News.

Sir,—We notice an extract from a letter from Dr. W. R. E. Hodgkinson in your issue of May 24 (vol. lxxi., p. 248), in which he states that he has detected argon and possibly helium in gases evolved from euxenite and samarskite when heated *in vacuo*. In reference to this we think it right to state that we have examined upwards of twenty minerals, among others samarskite and euxenite, with the view of finding a source of helium. Those which Dr. Hodgkinson has examined contain helium in small amount, and argon, if present at all, is present in exceedingly small quantity, for its spectrum is not discernible under ordinary circumstances. Indeed, we have found no mineral which gives an undoubted argon spectrum, but many which contain helium. It is impossible to conceive how Dr. Hodgkinson should have failed to see helium, for its spectrum appears in full brilliancy.

We have no desire and no right to ask Dr. Hodgkinson to discontinue his experiments, but as we should like to be allowed to publish our results *en bloc*, instead of producing them piecemeal.—We are, &c.,

W. Ramsay,
J. Norman Collie.

University College, London,
Gower Street, W.C., May 25, 1895.

"STEEL WORKS ANALYSIS."

To the Editor of the Chemical News.

Sir,—In Prof. Arnold's new work on "Steel Works Analysis," he refers to my volumetric process of determining chromium, and in introducing some modification of it offers some criticisms to which you will perhaps allow me to refer.

The modifications which he introduces seem so trivial and unusual, if not unfair, that they call, I think, for some reference or protest.

The process which he criticises was described in the Chemical News in 1877 (vol. xxxv., p. 151), while another paper on it (on account of his criticism) was read before the Iron and Steel Institute, in May, 1893, and about the same time before the Sheffield Metallurgical Society. His first objection, that chromium irons do not dissolve completely in the sulphuric acid, is a criticism which he has offered before, but the process at that time was never meant for rich chromium irons, as no such thing existed at the time. I do not know if Prof. Arnold really intends what he says on this point to be a "modification." He starts with 60 c.c. of water and 10 of sulphuric acid, as I also proposed in the original article, but states that it is necessary to boil until crystals of iron separate out, which it does after boiling about half an hour in an uncovered flask. It would scarcely be an objection, I think, to Prof. Penny's bichromate process of determining iron that some ores do not quite dissolve completely in hydrochloric acid, nor would it constitute a 'modification" to boil (and say crush the ore very fine) for an hour, supposing Prof. Penny had said half an hour.

His second objection is—

> "No precaution was given with reference to the vital-point of the vol. to which the solution must be diluted to ensure the oxidation of the chromium oxide."

In the original paper I say: "Dissolve in 6 parts of water and 1 of sulphuric acid." Prof. Arnold's modification consists in dissolving in 60 c.c. water and 10 c.c. sulphuric acid, and, after boiling till the sulphate of iron crystallises out, adding 100 c.c. water before adding the permanganate. Would not 130 c.c. water and 20 c.c.

sulphuric acid (allowing 20 c.c. for evaporation) be an equivalent?

So far as I am aware, Prof. Arnold has not shown that it is *necesssary* to dilute with this 100 c.c. water. Personally, I may say that after boiling I add some water, and will probably exceed 60 or 70 c.c. altogether, but that is done to simply add what was lost by evaporation.

How many c.c. water are necessary to constitute it a "modification"? I know some people who add 200 or 300 c.c. before adding the permanganate, and while I do not agree with them, they do not claim it as a "modification."

In his third objection, that "the amount of permanganate is six times too much," I think he is somewhat unfair. In 1877 the question was—"Would permanganate oxidise chromium oxide?" and to ensure that an excess was used. As time went on it was found that there was no fear of that, and hence an excess was not used, and the absence of any risk of non-oxidation was shown by Mr. Stead and myself in May, 1893, before the Iron and Steel Institute and the Sheffield Metallurgical Society. Yet he raises this objection in 1895. Prof. Arnold, at all events, is not entitled to any modification on this score.

Later on, Prof. Arnold writes:—"Mr. Galbraith has recently recognised this," and then he proceeds to refer to the "soda" modification which I mentioned in May, 1893. Now, this modification was introduced for irons rich in chromium, he criticises it under "Chromium Steel," for which it is quite unsuitable, and omits it under "Chromium Irons." I think I am justified, too, in saying that anything that was "recognised" here was "recognised" before Prof. Arnold "discovered" it.

I might say a very good modification of the process was described by Mr. Stead at the same two meetings referred to, and which I sometimes use, and at times think is an improvement; for instance, where there is doubt as to whether *all* the chromium is dissolved.

I really cannot think Prof. Arnold had any intention of being anything but fair in his criticism of the process, he must forgive me, however (remembering that he has twice, at all events, tried to replace it with another method, and now seems anxious that it should live), if I am anxious that it should live on its own merits and am interested in any modification of it which might be introduced.—I am, &c.,

Wm. Galbraith.

Chesterfield, May 24, 1895.

ACTION OF ARGON UPON ORGANISMS.

To the Editor of the Chemical News.

Sir,—Have you met with any systematic research on the action of argon upon living organisms, and especially upon animals? Such investigations, if existing, must have been made abroad in some country where the ruling powers are less "abhold gesinnt" to science and its followers.—I am, &c.,

J. W. Slater.

FLIES AND MICROBES.

To the Editor of the Chemical News.

Sir,—In reply to the letter appearing in the Chemical News (vol. lxxi., p. 257), I may state that I was acquainted with the article in *Nature* of March 23rd, 1893, and with the experiments mentioned by "X. Y. Z."

From all the information I had been able to gather, it appeared to me that the observers quoted by "X. Y. Z." kept their flies after contact with the pathogenic organisms in an unnatural condition, viz., *in close confinement* under glass covers. By my experiments, with harmless but easily-recognised organisms, I endeavoured to get over this important defect, and ascertain for what length of time flies would carry infection when they were allowed *perfect freedom*; and this more natural condition I endeavoured to obtain by experimenting with the flies in large furnished rooms, kept at high temperature to insure the maximum activity of the insects. For very obvious reasons it would be undesirable to experiment in this manner with flies infected with pathogenic organisms. My exhibit at the Royal Society's Conversazione was merely intended to afford a simple optical proof of the reality of the dangers which the exact and difficult researches of Sawtschenko and others have proved flies capable of causing.—I am, &c.,

William T. Burgess.

Reigate Hill, Surrey,
May 28, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 19, May 13, 1895.

Thermochemical Relations between the Isomeric States of Ordinary Glucose.—M. Berthelot.—It is concluded that in the anhydrous state the change from glucose α to glucose β would absorb $-1{\cdot}55$ cal. The change of glucose γ into glucose β would absorb $-0{\cdot}67$ cal. In the dissolved state the differences are much smaller and scarcely surpass the limits of experimental error.

On Argon and Helium.—Prof. Ramsay.—(See p. 260).

On the Definite Combination of the Copper-Aluminium Alloys.—A Rectification.—H. Le Chatelier.—The author had previously announced the extraction from alloys containing an excess of aluminium a definite compound, AlCu. He is now inclined to foresee the existence of two definite compounds, Al_2Cu and $AlCu_3$. An ingot of equal weights of the two metals having been steeped for 24 hours in a solution of sodium chloride appeared unattacked.

Determination of Sulphur in Cast Metals, Steels, and Irons.—Louis Campredon.—This paper will be inserted in full.

Researches on Mercurous Chloride, Bromide, Iodide, and Oxide.—Raoul Varet.—For the formation (setting out from the elements taken in their actual state) of mercurous chloride, bromide, iodide, and oxide, we have the following values:—

Hg_2 liq. + Cl_2 gas = Hg_2Cl_2 solution evolves $+62{\cdot}63$ cal.
Hg_2 liq. + Br_2 liq. = Hg_2Br_2 sol. $+49{\cdot}05$ cal.
Hg_2 liq. + I_2 sol. yellow amorphous $+28{\cdot}85$ cal.
Hg_2 liq. + I_2 solid greenish yellow amorphous $+28{\cdot}85$ cal.
Hg_2 liq. + O gas = Hg_2O sol. $+22{\cdot}17$ cal.

Molecular Origin of the Absorption-bands of the Salts of Cobalt and Chrome.—A. Etard.—The author concludes that—1. The salts of chrome and the red salts of cobalt present, after the manner of the rare earths and the salts of uranium, five spectral bands. 2. The spectra of these metals at least are molecular spectra like those yielded by organic matters such as the chlorophylls. 3. The hypothesis that to each band of the spectrum of a rare earth there must correspond an element is not necessarily true, as in the instance of cobalt. 4. The bands for one and the same element may be strikingly displaced or may cease to exist, according to the nature of the molecules in solution or of the compound observed.

Molecular Modifications of Glucose.—C. Tanret.—This memoir is not adapted for abstraction.

Use of Carbon Chloride as Agent for Separating Methylene from Ethylic Alcohol.—Maxime Cari-Mantrand.—The process is founded on the solubility in carbon tetrachloride, CCl_4, of the pyrogenous impurities of commercial methylenes, and on the separation of acetone and methylic alcohol mixed with vinic alcohol by distillation in presence of an alkaline chloride.

Brown Pigment in the Elytra of Curculio cupreus.—Dr. A. B. Griffiths.—The author obtains the pigment by extraction with boiling alcohol and ether. The product has the composition $C_{15}H_{13}NO$. It is soluble in alcohol, ether, and acetic acid. The solutions are gradually decolourised by light, and on spectroscopic examination do not give characteristic absorption-bands. The author names this pigment provisionally *cupreine*.

Aëration of the Soil in the Promenades and Plantations of Paris.—Louis Mangin.—The author ascribes the languid state of the ailanthus trees and the elms in and near Paris to deficient oxygenation of the soil and not to the infiltration of coal-gas.

MISCELLANEOUS.

Chemical Society in Milan.—A society has just been formed in Milan, to be known as the Società Chimica Milano, to be devoted to the encouragement of chemistry in all its branches.

Chemistry in Finland.—At the instance of the Academical Senate the Finnish Government has voted an annual sum of 5000 Finnish marks as the salary of a professor of chemistry at the Helsingfors University, as also an annual sum of 3000 Finnish marks in support of a hygienic laboratory. The Government has also subscribed a sum of 170,000 Finnish marks towards the cost of extending the pharmaceutical and physiological chemical laboratory.

Action of Ferric Acetate upon Potassium Iodide and Hydriodic Acid.—K. Seubert and Rud. Rohrer.—Ferric acetate and potassium iodide, either in a neutral or a strongly acetic solution, do not react in such a manner as to liberate iodine. But if free hydrochloric or sulphuric acid is added with a proportion of 3 equiv. of these acids to 1 mol. ferric acetate, in time almost the same quantities of free iodine is obtained as on the use of an equiv. quantity of ferric chloride or sulphate. The quantity of iodine ultimately set at liberty increases with the avidity of the acid present in the ferric salt.—*Zeit. Anorg. Chem.*, vii., Part 6.

Mason College, Birmingham.—Endowment of Research Scholarships.—We have received a notice concerning three "Priestley" Scholarships in Chemistry," two "Bowen" Scholarships in Engineering and one in Metallurgy, which have been founded by the late Mr. T. Aubrey Bowen, of Melbourne. They are intended to encourage and afford facilities for the higher study of these subjects in Mason College, where they are tenable for one year, with the possibility of renewal at the discretion of the Council of the College. The annual value of each is £100. Although, naturally, good work done at Mason College will be regarded as a specially favourable qualification, the Council have generously thrown all the Scholarships open to general competition. The first award will be made in September next, and all particulars may be learned on application to the Secretary of the College.

MEETINGS FOR THE WEEK.

Tuesday, June 4th.—Royal Institution, 3. "Thirty Years' Progress in Biological Science," by Prof. E. Ray Lankester, F.R.S.

Wednesday, 5th.—Geological, 8.

Thursday, 6th.—Chemical, 8. "On the Molecular Refractions of Dissolved Salts and Acids," by Dr. Gladstone, F.R.S., and W. Hibbert. "A Comparison of some Properties of Acetic Acid and its Chloro- and Bromo-Derivatives," by Spencer Pickering, F.R.S. "$\beta\beta$-Dinaphthyl and its Quinones," by F. D. Chattaway, D.Sc, Ph.D.

— Royal Institution, 3. "The Instruments and Methods of Spectroscopic Astronomy," by William Huggins, D.C.L., F.R.S.

Friday, 7th.—Royal Institution, 9. "Phénomenès Physiques des Hautes Régions de l'Atmosphère," by Prof. Alfred Cornu, D.C.L., F.R.S.

— Geologists' Association, 8.

— Quekett Club, 8.

Saturday, 8th.—Royal Institution, 3. "Elizabethan Literature," by Prof. Edward Dowden, D.C.L.

Erratum.—In Mr. Aslanoglou's letter on "Test for Morphia in Urine," p. 257, col. 2, *for* "100 parts" *read* "100,000 parts of water.",

THE CHEMICAL NEWS.

Vol. LXXI., No. 1854.

NOTE ON GASES OF THE HELIUM AND ARGON TYPE.

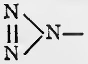
By BOHUSLAV BRAUNER, Ph.D., F.C.S.

Many years ago I obtained, on treating the mineral cerite with sulphuric acid and then with water, a gas showing the negative behaviour of nitrogen and containing some gas like hydrogen. I told this observation to Professor Ramsay two months ago, and I hope that he will not regard my experiments as a kind of trespassing on his field of investigation, especially as my experiments are only of a qualitative character. From that point of view I intended to decide the question whether helium, which is contained in clèveite—a mineral containing uranium and the rare earths—is associated with the first or the second class of substances in other minerals.

On heating the mineral cerite in a vacuum alone or with a sulphate a mixture of gases was obtained belonging, undoubtedly, to the helium and argon type, and showing in a Geissler tube a spectrum extremely rich in lines, which I shall describe fully later on. The same was observed with several Bohemian uranium ores. It is very likely that some of the cerite metals, like uranium, are elements with the highest atomic weights, and that they are found in the interior of the earth, being associated with gases of the helium and argon type.

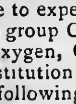
Professor Ramsay's classical research on the density of helium throws some light on the probable nature of helium and argon. Helium is, after, hydrogen, the lightest of all gases. The researches on the spectrum of helium from different sources (Lockyer) shows that it is a mixture of gases, just as argon is, and that they have one common constituent. If this common constituent is heavier than pure helium and lighter than pure argon, it is not impossible that pure helium is H_3, and pure argon N_3. It has been shown most ably by Mendeleeff that the argument derived from the relation of specific heats, $=1{\cdot}66$, is not absolutely conclusive in favour of the monoatomicity of the gases in question.

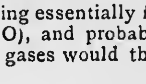
Professor Ramsay possesses important arguments against the assumption of the group—

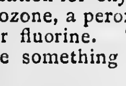


in argon, and, in fact, it is impossible, with our present ideas on "valency" and "bonds," to explain a constitution of molecules composed of "perissads" as H_3 and N_3. When we consider that Mendeleeff could write his "Principles of Chemistry" without taking "valency" and "bonds" as a basis, we shall have to look for a new mode of explanation of the constitution of the gases of the new type, before admitting that they contain new elements with the atomic weights 7·6 and 39·6, for it is highly improbable, as shown in a former note, that a new gaseous element having the boiling-point −187° can be placed between chlorine and potassium.

If it should be possible to prove that helium and argon are peculiarly condensed hydrogen and nitrogen we shall have to expect a similar mode of condensation for oxygen (the group O_3 differing essentially from ozone, a peroxide of oxygen, $O{=}O{=}O$), and probably for fluorine. The constitution of the gases would then be something like the following:—







&c.

Addendum, June 2.—The gas obtained by evacuation of pitchblende (uranine) of Pribram shows a peculiar behaviour. When brought into a Geissler tube with aluminium electrodes it emits, with a feeble current, a blue-violet light; with a stronger current, a crimson light; but never the beautiful golden-yellow fluorescing glow which so much struck me when I was happily present at the discovery of helium by its spectrum, in Professor Ramsay's laboratory, on March 22nd, afternoon. With the spectroscope used, the spectroscope shows the characteristic yellow line D_3, lying a little more to the refrangible end than the double distance of D_1, and D_2 is seen distinctly, together with nineteen other lines or groups of lines, three lines belonging to hydrogen, and only one of the strong lines in the red distinctly to argon. After observing the electrised Geissler tube for some time the helium lines disappear entirely, one by one; then the hydrogen lines begin to vanish; and an extremely feeble but characteristically fluted hydrocarbon spectrum, which was hitherto invisible, makes its appearance. The fact that helium is absorbed by aluminium seems to prove its metallic character and confirm the supposition—

$$He : H = A : N.$$

CLASSIFICATION OF THE CHEMICAL ELEMENTS.

By LECOQ DE BOISBAUDRAN.

The author states at the outset that, in consequence of an oversight, he has omitted to forward the following memoir to the Secretary. But the results had, he tells us, been communicated some weeks ago to M. Friedel and M. Demarçay.

In the calculation of the atomic weights of the elements of a hypothetical family which might be introduced into the Table of Mendeleeff, forming there an eighth column, I considered in my communication to the Academy (*Comptes Rendus*, Feb. 18, 1895, p. 361) only the substance, 20·1 ($O=16$), and its higher neighbours; that is to say, the only elements which can be introduced into Mendeleeff's eighth column, after eliminating those which rank there already, but which do not seem to me to belong to this family. Still my classification indicates the possible existence of an element ranking below the substance 20·1, with an atomic weight bordering very closely upon 3·9 ($O=16$). Also in the family of the halogens there is room for an element below fluorine, with an atomic weight very close upon 2·9 ($O=16$). It seems to me not useless to point out now these indications of the theory.

If we admit the real existence of the element 3·9, we are led for the substance 20·1 to an atomic weight differing but little from that which I have indicated.

I now learn that Prof. Ramsay, following up his magnificent discoveries, has determined the density of helium, referred to that of H, and finds it = 3·88. It is very remarkable that helium and argon give *for their densities* the same values which I find theoretically *for the atomic weights* of hypothetical elements which seem to agree with them.

By doubling the numbers 3·88 and 20 we should obtain atomic weights which seem difficult to place in a classification.

However, I am about to attempt here a very brief sketch of my classification, reserving for a future occasion the details and the exposition of numerous regularities, an account of which would be too tedious for this first communication.

At the outset of my researches I remarked that in each well-established natural family there exists a substance which, so to speak, summarises the characteristic properties of the family, of which it is, as it were, the centre, the *node*. I place then on the same plane the bodies of this nature, *i. e.*, Ca, K, (? δ *), Cl, S, P, Si, Al. The plane of these substances is, in fact, the upper limit of the increases of atomic weights near to 16, and the lower limit of the increases very approximately bordering on 48. Moreover, the superior triads attached to these substances are quite comparable among themselves, speaking chemically and even spectroscopically. To me the characteristic of these triads is the values of their variations, *i,e.*, the differences between the first increments bordering on 48 and the second. The values of these variations are comprised between very narrow limits.

If we place Mg and Na on the same plane as Al and Si, we compare—wrongly in my opinion—triads whose variations are very different (as well also as their chemical properties), and we then no longer find simple relations between the atomic weights of substances placed on the same plane, contrary to what holds good if we arrange the nodes as mentioned above. In this latter case we may calculate the atomic weight of a node by means of the atomic weights of the other nodes. Lastly, if we place Mg, Na, Si, P, Al, and S on the same line, we lose regularities which are useful for calculating the atomic weights of various nodes.

By means of the comparison of the variations I formerly calculated the atomic weights of gallium and germanium.

These principles lead to the following Table, considering in this preliminary paper merely the eight principal families :—

				(? η)''	Bi'	Pb''	Tl'	
Ba''	Cs'	(? ζ)	I'	Te''	Sb'	Sn''	In'	
Sr''	Rb'	(? ε)''	Br'	Se''	As'	Ge''	Ga'	
Ce''	K'	(? δ)''	Cl'	S''	P'	Si'	Al''	Nodes
Mg''	Na	(? γ)''	Fl'	O''	N	C''	Bo'	
Gl''	Li	(? β)''	(? α)'					
H	H	H	H	H	H	H	H	

All these families possess the same number of elements. The first substance of each family is derived from hydrogen.

The line of the nodes is the centre of the Table, setting out from H on the one hand, and from Bi, Pb, &c., on the other.

The nodes which have atomic weights greater than H by at least 32 may undergo two decreases of about 16 each, whence there are two substances between H on one side, and Ca, K, (? δ), and Cl on the other. The nodes which differ from H by less than 32 can undergo only one decrease of about 16, whence a simple substance between H on the one hand, and S, P, Si, and Al on the other.

But the families which have thus only a single substance below the node (H not included) receive an additional element above from the higher triad, with a large increase of atomic weight besides the highest body of the triad ; we find thus (? η), Bi, Pb, and Tl.

Setting out from hydrogen, each family therefore is formed by five successive increments, and the conditions are thus as if hydrogen itself resulted from another increment brought to a smaller element. There would be then from this hypothetical element, up to the planes Ba, Cs, ... Bi, Pb, six increments which we might suppose to correspond to the six surfaces of a cube, to the six directions of the three dimensions of space.

Recurrence, or periodicity, exists here ; it would exist, it is true, with any number of families, as if they continued to be constructed on the same plan without two great differences of increments from one plane to another.

The elements of even and odd atomicities alternate regularly from the smallest body to the largest.

The non-metals, or negative elements, occupy the centre ; the metals, or relatively positive elements, are placed at the extremities. In each of these classes the smallest element of each couple has a predominating odd atomicity ; the odd is more positive than the even, Ca'', K'—S'', P', &c.

This classification is compatible with the hypothesis that the chemical elements are in reality composed of portions of matter much smaller—far smaller even than hydrogen. This is Prout's law by extension. Provisionally, and as a maximum which I believe too high, I have adopted the $\frac{1}{128}$ of H for the unit employed in the calculations.

When once the nodes are classed according to the totality of the properties of the elements and according to the relations observed between the increments, the variations, &c., and when once the other planes are determined by the same procedure, we may thus theoretically represent the formation of the chemical elements.

Suppose a primordial mass of matter, A, which some unknown cause has just divided into two unequal portions. There will be produced on the same chemical plane two elements :—

$$\frac{A}{2} + q \text{ and } \frac{A}{2} - q ;$$

the one electro-chemico-positive in respect to the other. We have thus already a distinction between the metals and the non-metals, taking the sense of these words broadly. On splitting up anew each of these two bodies into unequal portions we obtain four elements, two of the positive and two of the negative series thus in succession. We have thus terms of transition between the most positive and the most negative elements. We confine ourselves for the present to consider eight substances thus formed. These substances, by means of successive increments or decrements, will give rise to the eight families of the foregoing Table. These increments and decrements will correspond to variations of the positive and negative characters in the perpendicular as well as in the horizontal direction of the Table. We see that the number of the families must be even.

The formation of the elements must depend therefore on the introduction of inequalities between the masses of matter, just as forces result from inequalities in the movements of bodies. In each case then is compensation, 1+ and 1− around an equilibrium which when once disturbed is never re-established. The fiction by which we may represent the formation of the elements by the unequal division of a primitive mass of matter is doubtless imaginary. Inequality must have existed from all eternity in so-called material masses, as well as in motions, by reason of a necessity always present, the cause of which escapes us. But is it not permissible for us to suppose that the material inequalities which represent the elements may be modified as do the *vires vivæ*, though their sum always remains constant ? Hitherto no satisfactory sign of a transformation of the elements, the one into the other, has been observed ; but I remain convinced that such a transformation is realised daily in Nature, under the influences of forces or of time, of which we are unable or ignorant how to avail ourselves.

By means of empirical relations, rendered very probable by their simplicity, I have sought to deduce the atomic weights of the first elements of the vertical columns from the atomic weight of hydrogen, in order to obtain absolute values for these atomic weights instead of taking for the bases of calculation the best experimental determinations. The progress of the decrements of about 16, setting out from the nodes, gives entire multiples of H, the most approximations of the atomic weights of the lower elements. The corrections to be made of these entire numbers of H follow from relations which deserve further examination, but which appear to me very simple and to agree sufficiently with the atomic weights of Li and N as determined by Stas. One of these relations would lead to the following values :—

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* An unknown body seeming to belong to the family of argon. In a second note the author enlarges on the "triads."

	H=1.	O=16.
Be	9·0156250	9·05098
Li	6·9921875	7·01961
(? β)	3·8906250	3·90588
(? α)	2·9375000	2·94902
O	15·9375000	Base
N	13·9843750	14·03922
C	11·9453125	11·99216
B	10·9218750	10·96471

Many elements may be classed according to the same principles, and following other rules the exposition of which would lead me too far. There are, however, bodies whose functions we do not know sufficiently to fix their places; we should be in danger of falling into the arbitrary.

Convinced that my attempt at classification is imperfect and incomplete, I express here the hope that it may one day experience the necessary modifications and improvements, and I shall consider myself happy if I can contribute in part to the correction of the errors almost inevitable in an investigation of this nature.

MM. Friedel and Moissan have on several occasions, and already a long time ago, heard M. Lecoq de Boisbaudran expound to them the considerations and the results which he now submits to the Academy. M. Friedel remembers having often heard M. de Boisbaudran quote, some days before the session of April 22, in which he has spoken of the atomic weights of the new elements *argon* and *helium*, the numbers 20 and 3·9 as to be probably assigned to them.—*Comptes Rendus*, cxx., No. 20, p. 1097.

THE ACTION OF HEAT UPON ETHYLENE.*
II.

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

N a paper communicated to the Royal Society in the spring of 1894 (*Roy. Soc. Proc.*, lv., p. 90; Chem. News, lxix., p. 87), I showed that ethylene, when subjected to heat, was converted into acetylene and methane, according to the equation—

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$

and that the acetylene so formed either at once polymerised, forming a large number of secondary products, or else decomposed to carbon and hydrogen, according to the temperature at which the action was being carried on.

The fact that ethylene is one of the principal products in many cases of destructive distillation renders a knowledge of the conditions affecting these changes of considerable importance, and the experiments described in this paper were made with the view of ascertaining the effect of rate of flow, area of heated surface, and dilution upon the changes taking place.

The apparatus and methods of analysis employed were the same as described in the former paper, with the exception that a platinum tube 14 m.m. in diameter and 73·6 c.m. long, was used as the decomposing chamber, and that an easily regulated gas combustion furnace was employed as the source of heat. The temperature of the gas in the tube was measured, as before, by the Le Chatelier thermo-couple, and every precaution was taken to keep it constant during the experiments.

The ethylene in each case was prepared by heating a mixture of 25 parts, by weight, of alcohol and 150 of strong sulphuric acid, purifying, and storing in a large glass holder.

The first set of experiments was to ascertain the influence of area of heated surface upon ethylene when passing through a tube heated to the temperature most often employed in the destructive distillation of coal and hydrocarbon oils, and also to find the result of varying the rate at which the gas was passed through the zone of heat.

Table I.

Influence of Rate of Flow and Length of Heated Surface upon the Amount of Ethylene Decomposed.

Temperature, 900° C. Rate of Flow, 5 c.c. per min.

Length of tube heated.	1 inch.		6 inches.		18 inches.	
Volume of gas—						
Before heating..	525		625		625	
After heating ..	490		653		670	
Analysis of Gaseous Products.						
Carbon dioxide ..	0·75		0·50		0·75	
Oxygen	0·50		0·25		1·00	
Unsaturated hydrocarbons	17·80		10·75		2·75	
Carbon monoxide	2·21		1·75		1·75	
Saturated hydrocarbs. by absorp.	11·25	46·87	9·50	60·75	12·22	65·42
Do. by explos.	35·62		51·25		53·20	
Hydrogen	24·12		22·75		24·00	
Nitrogen	7·75		3·25		4·33	

On now calculating the percentage for the change in volume, we obtain the following figures:—

Length of tube heated.	1 inch.	6 inches.	18 inches.
Unsaturated hydrocarbons	16·60	11·25	2·94
Saturated hydrocarbons	43·72	63·42	70·13
Hydrogen	22·50	23·75	25·72

The original gas, however, only contained 96·7 per cent of ethylene, so that the percentage of unsaturated hydrocarbons decomposed are:—

Length of tube heated.	1 inch.	6 inches.	18 inches.
	80·1	85·48	93·76

Table II.

Temperature, 900° C. Rate of Flow, 15 c.c.

Length of tube heated.	1 inch.		6 inches.		18 inches.	
Volume of gas—						
Before heating..	683		600		600	
After heating ..	615		515		640	
Analysis of Gaseous Products.						
Carbon dioxide ..	0·20		1·00		0·50	
Oxygen	0·50		0·50		0·75	
Unsaturated hydrocarbons	28·75		20·15		6·00	
Carbon monoxide	1·50		1·50		1·75	
Saturated hydrocarbs. by absorp.	8·80	42·25	9·43	51·81	19·22	56·72
Do. by explos.	33·45		42·37		37·50	
Hydrogen	21·15		20·55		28·75	
Nitrogen	5·65		4·50		5·53	

On now calculating the percentage for the change in volume, we obtain the following figures:—

Length of tube heated.	1 inch.	6 inches.	18 inches.
Unsaturated hydrocarbons	25·87	17·28	6·39
Saturated hydrocarbons	38·02	44·44	60·46
Hydrogen	19·03	17·63	30·64

The original gas contained 96·7 per cent of ethylene, so that the percentages of unsaturated hydrocarbons decomposed are—

Length of tube heated.	1 inch.	6 inches.	18 inches.
	70·83	79·42	90·31

(To be continued.)

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* A Paper read before the Royal Society.

ON THE
ESTIMATION OF CYANOGEN IN IMPURE SOLUTIONS, PARTICULARLY THOSE CONTAINING ZINC.

By J. E. CLENNELL, B.Sc.,
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It is a common complaint among those who have to do with the extraction of gold by the cyanide process, that the amount of cyanide in a given solution cannot be accurately determined, owing to the presence of various impurities in suspension or solution. The indications by the ordinary method of titration with silver nitrate are both indefinite and erroneous. Various suggestions have been made for overcoming this difficulty. As the matter is one of considerable technical importance, we thought it worth while to make an examination of some of the proposed methods. Those which we shall describe are—

1. Preliminary treatment with lime.
2. Titration with iodine.
3. Precipitation of the impurities by alkaline sulphides.

A. *Preliminary Treatment with Lime.*

Solutions are frequently met with containing exceedingly fine matter in suspension, which cannot be rendered clear even by repeated filtration. Such solutions are frequently treated by agitation with caustic lime, which causes a deposition of the suspended matter in a flocculent condition, in which state it can be readily removed by filtration. Lime has practically no action on alkaline cyanides; but there is of course a small error introduced, owing to the change of volume due to the dissolved lime. This, however, is negligible.

This method was found to yield accurate results only when the solution contained no soluble double cyanides. It may be employed with advantage when the liquid is turbid from the presence of finely-divided silica, oxide of iron, alumina, or other inert substance in suspension. Some double cyanides, such as that of zinc and potassium, are partially decomposed with precipitation of hydrate, $K_2ZnCy_4+Ca(OH)_2=Zn(OH)_2+2KCy+CaCy_2$, but the reaction is never complete. The indications obtained after such treatment are valueless, because, although the addition of caustic alkalies sets free some of the combined cyanide, and so raises the apparent strength of the solution, it does not enable us to determine the total amount of cyanogen. In solutions containing zinc the end-point is always preceded by the appearance of the characteristic flocculent precipitate of zinc cyanide ($ZnCy_2$).

Two solutions from the "zinc boxes" were tested, with the following results:—

(The silver nitrate solution was of such a strength that 1 c.c. = 0·01 grm. KCy.)

No. 1.

	Without lime.	With lime.
First turbidity with $AgNO_3$, 25 c.c. taken for test ..	0·9 c.c.	1·05 c.c.
Indicated strength	0·036 p. c.	0·042 p. c.

No. 2. 20 c.c. taken for each test.

	$AgNO_3$ required for first turbidity.	Indicated strength.
Without lime	0·4 c.c.	0·02 p. c.
With 0·1 grm. lime ..	1·5 ,,	0·075 ,,
,, 0·5 ,, ..	2·0 ,,	0·1 ,,
,, 1·0 ,, ..	2·0 ,,	0·1 ,,

B. *Titration with Iodine.*

Turbid solutions, if free from zinc, may in many cases be accurately titrated, without filtering, by the method of Fordos and Gelis. A solution of iodine in iodide of potassium is standardised against a solution of pure potassium cyanide, the strength of which has been accurately determined by the silver nitrate method. The end-point of the iodine reaction is marked by the appearance of a permanent yellow tint, or, if starch has been added, of a bluish-violet colour, and is in general very sharp and delicate. It is essential, however, that the solution shall contain no free caustic alkali or alkaline monocarbonate, as these bodies react with iodine, rendering the indications too high and also indefinite. It is generally recommended (see Sutton, "Vol. Anal.," 7th ed., p. 175) to remove the excess of alkali by the addition of soda-water (*i. e.*, a solution of carbonic acid); but this is troublesome, since any excess of carbonic acid will decompose cyanide with evolution of hydrocyanic acid.

The following simple method was found by the writer to give accurate results:—

Silver nitrate is first added to a measured volume of the solution to be tested until a permanent turbidity, or, if the solution was originally turbid, a distinct increase of turbidity, is observed. Addition of a few drops in excess is of no consequence. A drop of phenolphthalein indicator is now added to the same liquid, and the titration is continued with N/10 hydrochloric acid, until the pink colour disappears. Another measured portion of the original solution is then taken, and a trifle less than the quantity of hydrochloric acid shown to be necessary by the previous experiment for neutralisation of the alkali is added, drop by drop, with agitation. The solution is now ready for titration with iodine.

This process depends upon the following considerations:—

1. In a mixture containing alkaline cyanides, hydrates, and monocarbonates, the hydrates are converted into neutral salts, and the monocarbonates into bicarbonates, by the addition of a dilute mineral acid, before any of the cyanides are decomposed.
2. Bicarbonates of the alkali-metals are without action upon iodine.
3. When the cyanide in such a mixture has been converted into a double silver salt, the titration with dilute hydrochloric acid, with phenolphthalein as indicator, indicates the quantity required to neutralise the hydrates and convert the carbonates into bicarbonates (see Chem. News, Feb. 22, 1895).

The following experiments illustrate the effect of caustic alkalies on the indications by the iodine method of titration:—

No. of Expt.	Vol. of 0·05 p.c. KCy.	Vol. of N/10 KOH added.	Vol. of Iodine required.	Indicated strength of KCy.	Remarks. (1 c.c. Iodine=0·0035 grs. KCy.)
1	10 c.c.	—	1·4 c.c.	0·049 %	End-point quite definite.
2	10 ,,	5 c.c.	1·6 ,,	0·056 ,,	,, indefinite.
3	10 ,,	10 ,,	1·9 ,,	0·066 ,,	,, ,,
4	10 ,,	15 ,,	?	?	Faint yellowish tint beginning, about 1·6 c.c. End of reaction quite impossible to determine.

The effect of neutralising the alkali by the addition of hydrochloric acid is shown by the following experiments:—

A. A mixture of pure cyanide and caustic potash was prepared.

a. 10 c.c required 3·7 c.c. standard iodine, the end-point being somewhat indefinite.

b. 10 c.c. required 1·15 c.c. standard silver nitrate. On adding phenolphthalein and titrating with N/10 hydrochloric acid 5·75 c.c. were required.

c. 10 c.c. were mixed gradually with 5·5 c.c. of N/10 hydrochloric acid and the mixture titrated with iodine. 3·3 c.c. were required, the end-point being quite sharp.

d. 10 c.c. were mixed gradually with 5·5 c.c. of N/10 hydrochloric acid, and the mixture titrated with standard $AgNO_3$. 1·15 c.c. were required.

In these experiments—

1 c.c. standard $AgNO_3$ solution = 0·01 grm. KCy
1 ,, ,, iodine ,, = 0·0035 ,,

Hence the calculated percentage of cyanide in the four experiments above is as follows:—

a	0·1295 per cent
b	0·1150 ,,
c	0·1155 ,,
d	0·1150 ,,

B. An impure solution was titrated with the following results:—

a. 10 c.c. titrated with $AgNO_3$ gave a faint indication of turbidity with 1·6 c.c., distinct turbidity with 1·9 c.c. (indicating 1·6 per cent—0·19 per cent KCy).

b. 10 c.c. titrated direct with iodine required 6 c.c. (indicating 0·21 per cent KCy).

c. 10 c.c. were taken and 2 c.c. $AgNO_3$ added. This mixture was titrated with N/10 hydrochloric acid, using phenolphthalein indicator. 1·7 c.c. were required.

d. 10 c.c. were taken, and 1·5 c.c. N/10 hydrochloric acid added. This solution was then titrated with iodine, 5·95 c.c. being required (indicating 0·208 per cent KCy).

C. A mixture of cyanide and carbonate gave the following results:—

a. 25 c.c. required 1·1 c.c. $AgNO_3$ to give a permanent turbidity (indicating 0·044 per cent KCy). On continuing the titration with N/10 hydrochloric acid 4·6 c.c. were required.

b. 25 c.c. were taken, and 4·5 c.c. N/10 hydrochloric acid added. This mixture required 1·1 c.c. $AgNO_3$ (indicating 0·044 per cent KCy).

c. The same mixture required 3·65 c.c. iodine (1 c.c. iodine = 0·00323 grm. KCy). The indication, therefore, represents 0·047 per cent KCy.

D. Another mixture of cyanide and carbonate gave the following results:—

	No. of test.		
	1. C.c.	2. C.c.	3. C.c.
Volume of mixture taken	25	25	25
Volume of N/10 hydrochloric acid added	—	16	16
Volume of standard $AgNO_3$ required	1·0	1·05	—
Volume of standard iodine required	—	—	3·0
Indicated percentage of KCy ..	0·04	0·042	0·039

Test No. 1 was titrated with N/10 hydrochloric acid after addition of $AgNO_3$. 16 c.c. were required to destroy the phenolphthalein colour.

Solutions containing zinc did not give satisfactory results when titrated with iodine. In the first stage of the titration a faint yellowish tint appears in the solution, which is succeeded by a white flocculent precipitate. The first appearance of this precipitate was generally difficult to detect, but, in some instances at any rate, it appeared to correspond with the formation of a similar precipitate when silver nitrate is used, and therefore probably indicates the completion of the reaction—

$$KCy + I_2 = KI + ICy,$$

and the commencement of the decomposition of the double cyanide according to the equation—

$$K_2ZnCy_4 + 2I_2 = 2KI + 2ICy + ZnCy_2.$$

After the formation of this precipitate the solution becomes colourless. On further addition of iodine, the amount of the flocculent precipitate continually increases until, at a certain stage, also very indefinite, the yellow colour reappears. The following results were obtained in testing various solutions containing zinc by both methods:—

		Percentage of KCy indicated.		
		By $AgNO_3$.	By Iodine.	
No. of test.		First precipitate.	First precipitate.	Permanent yellow tint.
1.	Weak solution ..	0·026	0·026	0·142
2.	,, ,, ..	0·036	0·035	0·079
3.	Strong solution ..	0·260	0·232	0·283
4.	,, ,, ..	0·275	0·238	0·312
5.	,, ,, ..	0·275	0·240	0·310

C. *Precipitation by Alkaline Sulphides.*

The methods given in the various text-books for estimating cyanogen in double cyanides are, as a rule, tedious, and involve a number of separate operations, some of which occupy a considerable amount of time. The following method, while it is not applicable to every possible case, is fairly rapid, and serves to determine the "total cyanide" (*i.e.*, the whole of the cyanogen, estimated as its equivalent of potassium cyanide) in solutions commonly met with, particularly such as contain zinc. It depends upon the following facts:—

1. That many double cyanides, such as those of zinc, silver, mercury, &c., are decomposed by sulphuretted hydrogen or an alkaline sulphide, with precipitation of the metal as sulphide (see Valentine, "Qual. Anal.").

2. That the excess of sulphide may be removed without affecting the cyanides by the addition of insoluble compounds of lead, such as the oxides, carbonate, &c. (see Fresenius, "Quant. Anal.," vol. i., p. 375).

The method is as follows:—A measured volume of the solution is made strongly alkaline by the addition of caustic potash or soda. Sulphuretted hydrogen is passed into the liquid until it ceases to give a precipitate, avoiding a large excess, or, which is better, a concentrated solution of pure sodium sulphide is added in slight excess. The solution is then well shaken and allowed to stand until the precipitate has subsided. A little lime may be added to assist the settling of the precipitate, in which case it can be filtered without difficulty. The clear filtrate is freed from excess of sulphide by agitating with litharge, which is best added in small quantities at a time, with constant agitation, until a drop of the liquid no longer gives the slightest black or brown colouration with a drop of lead acetate solution. A definite volume is then filtered off, and tested with silver nitrate in the ordinary manner.

Another method (which is not perfectly accurate, as the volumes occupied by the precipitated sulphides, and the excess of lead carbonate are neglected) is as follows. It is accurate enough for most practical purposes:—After precipitation with sulphuretted hydrogen or sodium sulphide, the liquid is made up to a definite volume, say 100 c.c., and, after settling, a measured volume of the clear liquid (say, 50 c.c. or 25 c.c.) is taken, and added, with agitation, to a freshly prepared mixture of lead acetate and sodium carbonate, in which an excess of sodium carbonate is present. Sufficient lead must be present (as carbonate) to convert the excess of sodium sulphide into lead sulphide and sodium carbonate. The liquid is again made up to a definite volume and allowed to stand. The precipitate settles very rapidly, and a definite volume of the supernatant liquid is decanted off; filtering if necessary. This may now be tested with silver nitrate.

The liquid to be tested must fulfil the following conditions:—

1. It should give a perfectly white precipitate with a drop of lead acetate solution.
2. It should give no precipitate with sodium carbonate.
3. It should give no precipitate with sulphuretted hydrogen. A faint brown colouration is usually produced, probably owing to the solution of a small quantity of lead oxide or carbonate in the alkaline fluid.

In titrating with silver nitrate a slight granular precipitate was generally observed towards the finish. It was necessary to add the last few drops of silver nitrate slowly, with agitation. The end-point, however, was perfectly definite, the granular precipitate being disregarded. The point to be noted is the appearance of a distinct permanent turbidity pervading the whole liquid and not disappearing on standing.

The following experiments will illustrate the application of the method:—

a. A mixture was made of—
25 c.c. pure potassium cyanide (KCy=0·924 p.c.)
[*] 2 ,, zinc sulphate (1 c.c. = 0·01 grm. Zn)
10 ,, normal caustic potash
10 ,, concentrated sodium carbonate.

This mixture was precipitated by sulphuretted hydrogen, and the precipitate filtered off and washed thoroughly. The filtrate was mixed with sufficient lead acetate solution to precipitate the excess of sulphide, and made up to 100 c.c.

25 c.c. required 5·7 c.c. standard $AgNO_3$
" " 5·7 " "
Indicating 0·912 per cent KCy.

b. A mixture was made of—
50 c.c. pure potassium cyanide (KCy=0·924 p.c.).
10 c.c. pure zinc sulphate (1 c.c.=0·01 grm. Zn).
10 c.c. normal caustic potash.
10 c.c. concentrated sodium carbonate.

After passing in sulphuretted hydrogen, the liquid was made up to 100 c.c, After allowing the precipitate to settle, the supernatant liquid was filtered, and 25 c.c. of the clear filtrate were added to a mixture of lead acetate with excess of sodium carbonate. This was made up to 100 c.c. and filtered.

50 c.c. required 5·65 c.c. standard $AgNO_3$.
Indicating 0·904 per cent KCY.

c. A mixture was made of—
40 c.c. pure potassium cyanide (KCy=0·924 p.c.).
5 c.c. pure zinc sulphate (1 c.c.=0·01 grm. Zn).
20 c.c. normal caustic soda.

This was precipitated by sulphuretted hydrogen, diluted to 100 c.c., and agitated with a little caustic lime. After the precipitate had settled, 25 c.c. of the clear liquid were added to a mixture of lead acetate and potassium carbonate, in which the alkaline carbonate was in excess. The liquid was made up to 100 c.c. and filtered.

25 c.c. of the filtrate required 2·4 c.c. standard $AgNO_3$.
50 c.c. " " 4·75 c.c. " "
Indicating 0·955 per cent KCy.

d. A mixture was made of—
40 c.c. pure potassium cyanide (KCy=0·924 p.c.)
5 c.c. pure zinc sulphate (1 c.c.=0·01 grm. Zn).
20 c.c. normal caustic soda.

This mixture was precipitated with sulphuretted hydrogen, and the liquid diluted to 100 c.c. One grm. of caustic lime was added, and, when the precipitate had settled, 50 c.c. of the clear liquid were agitated with 25 grms. of litharge. The solution was then filtered.

25 c.c. required 9·35 c.c. $AgNO_3$.
25 c.c. ,, 9·25 c.c. ,,
Indicating 0·93 per cent KCy.

e. A mixture was made of—
40 c.c. pure potassium cyanide (0·924 per cent).
5 c.c. pure zinc sulphate (1 c.c.=0·01 grm. Zn).
20 c.c. normal caustic soda.

To this was added 5 c.c. of a concentrated solution of pure sodium sulphide, the liquid made up to 100 c.c., and settled with lime; 25 c.c. of the clear liquor were added to a mixture of lead acetate with excess of potassium carbonate. This was made up to 100 c.c. and filtered.

25 c.c. required 2·4 c.c. $AgNO_3$.
50 c.c. ,, 4·65 c.c. ,,
Indicating 0·945 per cent KCy.

Whenever the quantity of zinc was at all considerable it was found necessary—

1. To remove the precipitated zinc sulphide by filtration before addition of lead salts. (Even thoroughly washed sulphide of zinc reacts upon carbonate of lead with formation of lead sulphide).
2. To add an insoluble compound of lead, and not a solution of lead acetate. The latter would be liable to precipitate cyanide of lead.

Before precipitating with sulphuretted hydrogen it is necessary to add a considerable quantity of alkaline hydrate, or low results will be obtained, owing to the liberation of hydrocyanic acid. When an alkaline monocarbonate was substituted for the hydrate the results were not satisfactory.

Application of the Method to Solutions from the Zinc-boxes.

The solution tested had been used for fifteen successive washes on the same charge of material, and had been passed each time through the zinc-boxes. It was therefore highly charged with zinc, as well as various impurities extracted from the ore.

(*a*). Tested by direct titration with silver nitrate, 10 c.c. required 1·45 c.c. $AgNO_3$ to give the first sign of a permanent turbidity (indicating 0·145 per cent), and 1·7 to 1·8 c.c. to give a perfectly distinct turbidity. The "free cyanide" may therefore be taken as about 0·17 to 0·18 per cent.

(*b*). The same solution was tested in a variety of ways for "total cyanide," by the method described above. The following mixtures were made:—

	(i.)	(ii.)	(iii.)
Solution taken	40 c.c.	80 c.c.	40 c.c.
Normal caustic soda	20 ,,	10 ,,	10 ,,
Precipitant used ..	H_2S	H_2S	Na_2S
Indicated strength in KCy..	0·80 p.c.	0·77 p.c.	0·785 p.c.

Mean of all determinations, 0·789 per cent.

In each case the excess of sulphide was removed by means of a mixture of lead acetate with excess of potassium carbonate.

In a future paper I hope to be able to give particulars of a method successfully applied here for estimating cyanides and ferrocyanides in the same solution.

Johannesburg, April 16, 1895.

The late Prof. Neumann.—We regret to record the death of Geh. Rath. Neumann, Professor of Physics at the University of Königsberg, Prussia, at the advanced age of 97. Prof. Neumann was born in 1798, at Joachimsthal, near Berlin, and studied at Jena and Berlin. He became connected with the University of Konigsberg in 1826. His chief researches were in connection with specific heat, polarisation of light, and magnetism and electricity.

New Edition of "Bloxam's Chemistry."—Messrs. J. and A. Churchill announce a new edition, re-written and revised, of "Bloxam's Chemistry, Inorganic and Organic," by Prof. J. M. Thomson, of King's College, and Mr. A. G. Bloxam, Head of the Chemistry Department, Goldsmith's Institute. Several new woodcuts have been added. The same firm also announce as nearly ready a new work by Mr. Alfred H. Allen, entitled "The Chemistry of Urine, a Practical Guide to the Examination of Diabetic, Albuminous, and Gouty Urine," with illustrations.

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[*] Assuming that 1 part of zinc is capable of converting 4 parts of KCy into the double cyanide (K_2ZnCy_4), this solution should contain the equivalent of 0·08 grm. KCy as K_2ZnCy_4 and 0·151 grm. free KCy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 16th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Croysdale, The Grange, Whitley Bridge, R.S.O.; Joseph Lones, Lansdowne, South Road, Smethwick; Arthur E. Potter, M.A., B.Sc., Rangoon; E. J. Read, B.A., 2, Leigh Terrace, Bedford.

The following were duly elected Fellows of the Society:—Harold Allden Auden, B.Sc.; Edgar S. Barralet; Eugen Blume; Lancelot Alexander Borradaile, B.A.; Henry Bradford; Gustav Theodore Bruckmann, B.Sc.; Walter W. Cheadle, B.A.; Virgil Coblentz, Ph.G., A.M., Ph.D.; Herbert William Cook, B.Sc.; Edric Druce; Arthur T. Eutroppe; Sydney Fawns; Hasslewood Irving Foster; Alexander F. Fuerst, Ph.D.; John Francis Hutchins Gilbard; William Goddard; Patrick Hope Grant; William Abraham Greaves, B.Sc.; Alexander Gunn; H. Loft Haller; Evan Lewis Jones, B.A.; Robert Charles Marchant; Prosper Henry Marsden; John McGlashan; Robert Selby Morrell, M.A., Ph.D.; Charles Butterworth Newton; Lama Gray Patterson; George Elliott Shaw; Frank L. Slocum; Kekhasrie Engineer Sorabji; Thomas Coke Squance, M.D., M.S.; Alfred Stansfield, B.Sc.; Alfred F. Theodosius, B.A.; William Thomas Thomson; Arthur Thornton, M.A.; Frederick Gwilym Treharne; George John Ward; Arthur William Warwick; Henry F. A. Wigley, B.A.; William Arthur Whiston; John Wilson, B.Sc.

Of the following papers those marked * were read :—

*65. "*Kjeldahl's Method for the Determination of Nitrogen.*" By BERNARD DYER, D.Sc.

This method, variously modified, has, in most agricultural laboratories, superseded the well-known soda-lime method, over which it possesses marked advantages for the analysis of feeding-stuffs and fertilisers. It has not, however, been generally adopted by scientific chemists, and little information is available as to its applicability to different types of organic compounds. To supply such information was the object of the present investigation.

The best modification of the method, in the author's experience, for the analysis of feeding-stuffs and fertilisers not containing nitrates, and applicable, as will be seen, to a large number of organic compounds, is the Kjeldahl-Gunning method modified, however, by the use of mercury. A suitable quantity of the material to be analysed is mixed in a round-bottomed, hard glass flask, with 20 c.c. of strong sulphuric acid and a drop of mercury, and warmed for a short time, when 10 grms of potassium sulphate are added. The contents of the flask are then boiled until colourless. With many materials this result happens within half an hour, and it is rarely deferred beyond an hour. The contents are washed into a distilling flask, mixed with excess of soda and a little potassium sulphide (to decompose mercury compounds), and the ammonia then distilled off into standard acid, which is afterwards titrated in the usual way. No spray trap is necessary in distilling if the connection between the distilling flask and receiver is made by means of a long block-tin tube, rising perpendicularly 15 or 20 inches from the neck of the flask. The author prefers not to use a condenser, but to drive the steam directly into the standard acid, which stands in a trough of cold water, the delivery tube terminating in a pear-shaped glass bulb, to prevent regurgitation of the acid. The use of mercury is not necessary, but materially expedites the process.

When nitrates are present, or nitro-compounds and certain other compounds referred to in the paper, Jodlbauer's modification is used. This consists in dissolving in the sulphuric acid used for oxidation a small quantity (about 2 grms. for a single determination) of phenol or salicylic acid. The nitrogen in the nitrate or nitro-group then forms a nitro-compound with the sulphonated phenol or salicylic acid. In many cases it is highly important that the sulphuric acid containing the phenol or salicylic acid should be poured directly and suddenly on to the material contained in the flask, so as to submerge it immediately, and not to let it trickle from a pipette. If nitrates and ammonium salts are both present, loss of nitrogen occurs, unless this precaution is observed; this does not appear to be generally known, and probably often gives rise to errors. One or two grms. of zinc dust (as well as a drop of mercury) are dissolved in the contents of the flask while still cold. The process is then continued exactly as before.

The method first described as the "Kjeldahl-Gunning" method was found to give very nearly the exact percentages of nitrogen in uric acid, asparagine, caffeine, indigotine, morphine, quinine, strychnine, aniline, atropine, diphenylamine, naphthylamine, acetanilide, orthobenzoic sulphinide, sulphamido-benzoic acid, pyridine, benzidine, aldehyde ammonia, and nitroso-di-methyl-aniline.

The Jodlbauer modification referred to by the author as the "Kjeldahl-Gunning-Jodlbauer" method, was found to give nearly correct percentages of nitrogen in potassium nitrate, ammonium nitrate, urea nitrate, nitrobenzene, nitronaphthalene, nitraniline, dinitrobenzene, trinitrophenol, and potassium para-bromo-chlor-nitro-phenol.

It might be expected that reduction with zinc alone, without the use of phenol or salicylic acid, would suffice in the case of aromatic nitro-compounds. The author finds, however, that if zinc alone be used with aromatic nitro-compounds there is loss of nitrogen, as though it were necessary that more carbon should be present.

The Kjeldahl-Gunning method fails to furnish the calculated quantity of nitrogen in azobenzene or amido-azobenzene. The loss in the former case was small; in the latter case it amounted to nearly 50 per cent. Mere reduction by zinc suffices with amido-azobenzene, but in the case of azobenzene the complete Jodlbauer modification is necessary. With amido-azotoluene the correct amount was obtained by the Kjeldahl-Gunning process supplemented by reduction with zinc and with carbazol by the Kjeldahl-Gunning method alone.

Hydroxylamine hydrochloride, which contains 20·21 per cent of nitrogen, yielded only 3 per cent by the Kjeldahl-Gunning method; by reduction with zinc about 10 per cent was obtained; by the Kjeldahl-Gunning-Jodlbauer method about 19 per cent; by reduction with sugar and zinc less than 19 per cent. The Kjeldahl-Gunning-Jodlbauer method, with the addition of sugar as well as zinc, however, gave the calculated quantity in each of three separate determinations. Acetaldoxime, by the Kjeldahl-Gunning method, gave somewhat low results, but with the addition of sugar and zinc furnished correct results. Naphthoquinone-oxime yields its full percentage by the Kjeldahl-Gunning method.

Potassium cyanide and ethyl cyanide both give nearly correct results by the Kjeldahl Gunning method; no trace of hydrocyanic acid is evolved if the sulphuric acid used is strong. Potassium ferrocyanide also yields accurate results. Potassium ferricyanide, however, only gives sufficiently accurate results when reduced by the addition of sodium thiosulphate. Sodium nitroprusside failed with any modification of the method to yield all its nitrogen.

Phenyl-hydrazine derivatives cannot by any modification of the method tried by the author be made to give correct results; there is invariably loss of nitrogen, presumably liberated in the free state. The derivatives used were phenyl-hydrazinehydrochloride and glucosazone. Symmetrical di-phenyl hydrazine, or hydrazobenzene, affords accurate results with the Kjeldahl-Gunning method. This substance, however, ceases to be a hydrazine when dissolved in acid, as it is converted into benzidine which furnishes the calculated amount of nitrogen.

Discussion.

Dr. Kipping remarked that Dr. Dyer's results pointed to the conclusion that different types of organic compounds required special treatment in order to obtain the whole of the nitrogen as ammonia, whilst some compounds did not under any conditions furnish accurate results. The method could not therefore be regarded as a substitute for the absolute method of Dumas.

Mr. Hehner said that few analytical processes had been the subject of so much investigation as the Kjeldahl method, the original process having undergone very many modifications. Originally the oxidation was carried out only very partially by sulphuric acid, potassium permanganate being used as soon as the acid had produced charring. Kjeldahl had found that by the action of the acid alone only about 25 per cent of the total nitrogen in quinine, and about 40 per cent of the nitrogen in morphine, was obtained, whilst after the action of permanganate almost the whole of the nitrogen appeared as ammonia. The use of permanganate had already been recognised as leading to the loss of nitrogen, and Kjeldahl had himself pointed out that the heating after the addition of permanganate must be moderate, or loss may occur. Much of the ground occupied by Dr. Dyer's paper had already been gone over by others, especially by Arnold and Wedemeyer. Taking into account the results obtained by the various investigators of the process, it might be said that the Kjeldahl process, as modified by Wilfarth, Gunning, and Jodlbauer, was a most accurate and convenient one for the determination of nitrogen in naturally occurring nitrogenous substances, especially in feeding materials.

Dr. Morris considered that there was no doubt as to the value of Kjeldahl's process for determining nitrogen in proteids and similar nitrogenous compounds. He had found it advantageous to use permanganate as originally suggested by Kjeldahl.

Professor Dunstan suggested the stability of hydroxylamine sulphate as a probable explanation of the small amount of ammonia furnished by hydroxylamine salts in the absence of a special reducing agent. The subsequent action of alkali on the sulphate would liberate only a part of the nitrogen as ammonia. Similarly with oximes, some hydrolysis would occur, producing hydroxylamine sulphate, although here the decomposition of the hydrocarbon radicle would ensure nearly complete reduction of the oximido-group to ammonia.

*66. "*Note on Liquation in Crystalline Standard Gold.*" By T. K. Rose, D.Sc., A.R.S.M., Assistant Assayer of the Royal Mint.

It has been suggested by Roberts-Austen that, although no segregation occurs on the solidification of alloys of gold with silver and copper, some rearrangement might be expected to take place when these alloys are made crystalline and brittle by the addition of small quantities of bismuth or lead. The author accordingly rendered standard gold impure in three successive experiments by the addition of 0·2 and 0·4 per cent of bismuth and 0·2 per cent of lead respectively, casting the metal in a spherical iron mould, and assaying various parts of the mass.

The observed variations in the composition of different parts of the mass can be explained by assuming that in these alloys a saturated solution of gold and silver in bismuth or lead (no doubt containing a little copper in addition) remains molten after the greater part of the gold and copper has solidified. Those constituents which are the first to become solid are thus enabled to assume a definite crystalline form. Moreover, as the portion of the material which remains molten longest is pushed towards the centre of the mass during cooling, the interior is enriched in both gold and silver.

*67. "*Preparation of the Active Lactic Acids and the Rotation of their Metallic Salts in Solution.*" By T. Purdie, Ph.D., B.Sc., and J. Wallace Walker, M.A.

The authors have prepared the active lactic acids in considerable quantity by the process previously described (*Trans.*, 1893, lxiii., 1143), using certain modifications, and have used the material thus obtained for examining the optical activity of some of the metallic lactates in aqueous, alcoholic, and aqueous-alcoholic solutions of varying equivalent concentrations. The freezing-points of a number of the same solutions were also determined with the double object of obtaining an approximate estimate of the amount of dissociation attending the changes in molecular rotation, and of detecting the existence or non-existence of racemoid compounds in solution.

The salts examined were those of lithium, sodium, potassium, silver, calcium, strontium, barium, magnesium, zinc, cadmium, and zinc-ammonium.

All these salts in aqueous solution within the limits of concentration used were found to be active in the opposite sense to that of the acid from which they were prepared, and the activity was found to increase with dilution, except in the case of the silver salt, the rotation of which undergoes a slight decrease.

The salts of the alkaline metals comprising those of silver, also those of barium and strontium, tend to a common maximum molecular rotation of about 14·5°, an observation which is in accordance with the law of Oudemans. The salts of the other metals show divergencies from this law which indicate that the activity of their solutions cannot be accounted for by the presence of simple molecules and ions alone, but that it is probably largely influenced by the formation of molecular aggregates, whose activity differs widely from that of the other factors. This assumption is confirmed by observations of the rotation of the sodium and potassium lactates in alcohol and of other salts in aqueous alcohol.

A comparison of the freezing-points of solutions of active and inactive lithium and strontium lactates shows that the racemoid salts are resolved into their components in aqueous solution. The corresponding coefficients of depression of the barium salts show slight differences which may possibly be due to the presence of racemoid salt.

68. "*Derivatives of Succinyl and Phthalyl Dithiocarbimides.*" By Augustus E. Dixon, M.D., and R. E. Doran.

On heating together lead thiocyanate, succinyl chloride, and dry benzene, succinyldithiocarbimide is formed and goes into solution,—

$$C_2H_4(COCl)_2+Pb(SCN)_2=PbCl_2+C_2H_4(CO{\cdot}NCS)_2.$$

It is a pungently smelling, very unstable compound, soluble in all proportions in benzene, decomposed by water into succinic and thiocyanic acids, and easily desulphurised by silver or alkaline lead salts.

The benzene solution yields, on the addition of bases, the corresponding symmetrical dithioureas. From aniline, *succinyldiphenyldithiourea* was obtained,—

$$C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NHPh)_2.$$

This forms silky needles (from hot acetic acid), sparingly soluble in most solvents, and melting with decomposition at 210—210·5° (corr.). The compound is readily desulphurised by ammoniacal silver nitrate in the cold, or by warming with alkaline lead tartrate. It dissolves in warm dilute caustic alkali, thereby breaking up into phenylthiourea and succinic acid; and is decomposed by alcoholic ammonia, under pressure, forming phenylthiourea.

Succinyldiorthotolyldithiourea,—

$$C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NH\textit{o}\text{-}To),$$

similarly prepared from *o*-toluidine (yield = 96 per cent), formed colourless glassy needles, melting at 217—218°, and resembling in most other respects the corresponding phenyl compound.

Succinyldi-α-naphthyldithiourea was found to be practically insoluble in all the ordinary solvents: after washing with spirit, it formed a pure white powder melting at 224—225°, and desulphurised by lead or silver solutions.

From methylaniline, symmetrical *succinyldimethyldiphenyldithiourea* was obtained,—

$$C_2H_4[CO{\cdot}N{:}C(SH){\cdot}NMePh]_2,$$

deposited from hot alcohol in rosettes of needles, m. p. 137—138°; resembling the preceding compound in properties, and decomposed by warm dilute potash, forming unsymmetrical phenylbenzylthiourea (Werner, *Proc. C. S.*, 1892, 96).

Succinyldiphenyldisemithiocarbazide,—

$$C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NHPh)_2,$$

from the thiocarbimide and phenylhydrazin, occurred in crystals, melting at about 220°. With anhydrous alcohol, the thiocarbimide afforded the *dithio-diurethane*,—

$$C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}OEt)_2;$$

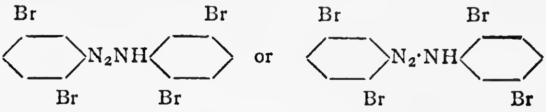
thick white prisms, insoluble in water, soluble in alcohol, desulphurised by warming with ammoniacal silver or alkaline lead solutions, and melting at 166—167°.

From phthalyl chloride and lead thiocyanate, similarly, a solution of phthalyldithiocarbimide was prepared; it appears to be a crystalline solid, but could not be obtained in a pure condition. With *water*, it yields phthalic and thiocyanic acids; and combines with bases, like the succinyl analogue, forming thioureas the examination of which is not yet complete. The *aniline* derivative melted at 209—210°; the *orthotoluidine* and *benzylamine* derivatives at 152—153° and 163° respectively. Secondary *butylamine* produced a red oil, and *methylaniline*, vitreous prisms melting at 184—185°, and decomposed by fuming nitric acid, with production of a tetranitromethylaniline, $C_6H_2(NO_2)_3{\cdot}NMe(NO_2)$, m. p. 127°.

69. "*The Action of Nitrous Acid on Dibromaniline*, $C_6H_3BrBr{\cdot}NH_2 = 1:4:2$." By Raphael Meldola, F.R.S., and Ernest R. Andrews.

During the course of some experiments on the dihaloid derivatives of β-naphthylamine which are still in progress it has been found that under certain conditions nitrous acid converts these compounds into diazoxides with the elimination of one atom of the halogen. In order to see whether this property was possessed by analogous compounds of the benzene series, paradibrombenzene was nitrated and converted by reduction into the dibromaniline, m. p. 51—52°, described by Meyer and Stüber (*Ann.*, clxv., 180). It is of interest to record that this dibromnitrobenzene cannot be reduced by zinc dust and acetic acid in alcoholic solution, in the same way that the corresponding naphthalene derivatives can be reduced to β-naphthylamine derivatives (Meldola and Desch, *Trans.*, 1892, 768). In order to effect complete reduction, it is necessary to boil the alcoholic solution with tin and hydrochloric acid in the usual manner.

The conditions favourable for the formation of diazoxides in the naphthalene series, are that the diazotising operations should be carried out in presence of an excess of strong sulphuric acid and that the diazo-salt should be warmed with dilute sulphuric acid to complete the transformation. If these conditions are not complied with the diazoamido-compound is formed instead of the diazoxide. In the present case, therefore, the dibromaniline was dissolved in glacial acetic acid, an excess of strong sulphuric acid poured in, and a little more than the calculated quantity of sodium nitrite added in small portions with constant stirring; the solution was kept cooled during this operation. When all the nitrite had dissolved, the solution was very gradually diluted with water; a clear liquid was obtained, and at this stage the solution no doubt contains the diazo-sulphate. On warming the solution for some hours nitrogen was evolved, and a brown substance separated out. The latter was not soluble to any extent in boiling water and did not therefore appear to contain a diazoxide; it was not dissolved in appreciable quantity by dilute alkali, and did not therefore contain anything phenolic. After many crystallisations from benzene, the compound was obtained in the form of brownish flattened needles melting at 234—235°. Analysis proved that it was the diazoamido-compound and that the formula was—



0·0838 gave 5·85 c.c. moist nitrogen at 12° and 752·3 m.m. N = 8·19.
0·0975 gave 0·1431 AgBr. Br = 62·46.

The formula requires N = 8·19 and Br = 62·38 per cent.

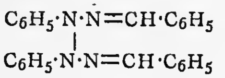
An attempt to transform this diazoimide into an amidoazo-compound was not successful; it decomposes very readily, forming dibromaniline, when treated with aniline and aniline hydrochloride in the usual way. The chief point of interest in the present note is the fact that dibromaniline so readily forms a diazoamido-compound in presence of an excess of sulphuric acid. Analogous experiments without this excess of acid have led to similar results with the corresponding dichloraniline, but these are not so remarkable under the conditions specified (Zettel, *Ber.*, 1893, 2471; and Herschmann, *Ber.*, 1894, 767).

Tribromaniline, $C_6H_2{\cdot}NH_2{\cdot}Br{\cdot}Br{\cdot}Br = 1:2:4:6$, also fails to give a diazoxide when diazotised in the presence of excess of sulphuric acid.

70. "*A New Modification of Benzilosazone.*" By Harry Ingle, Ph.D., B.Sc., and Harold H. Mann, B.Sc.

By the action of iodine on a mixture of benzalphenylhydrazone and sodium ethylate suspended in ether, the authors obtained two substances. On treatment of the mixture with ether or ethyl acetate, it was separated into its components.

The insoluble portion on re-crystallising from benzene was obtained in difficultly soluble, silky, yellow needles, melting at 186° C., identical with dibenzaldiphenylhydrotetrazone already described by Minunni (*Gaz. Chim. Ital.*, xxii., 2, 217), and by v. Pechmann (*Ber.*, xxvi., 1045), to which the formula—



$$\begin{array}{l} C_6H_5{\cdot}N{\cdot}N{=}CH{\cdot}C_6H_5 \\ \qquad | \\ C_6H_5{\cdot}N{\cdot}N{=}CH{\cdot}C_6H_5 \end{array}$$

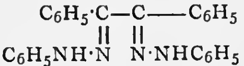
has been assigned.

On evaporating off part of the solvent and adding alcohol to the residue, the soluble portion separated as a yellow crystalline powder. This proved to be a stereoisomeride of benzilosazone, and since it is the least stable the authors have named it α-benzilosazone.

α-Benzilosazone crystallises from a mixture of benzene and alcohol in faintly yellow-coloured prisms, melting at 208° C. On heating its solution in ethyl succinate, benzoate, or malonate to the boiling-point, or by heating it in a sealed tube with alcohol to 210° C., it is changed into the normal or β-benzilosazone (m. p. = 225). Phenylhydrazine also brings about this change. When heated on the water-bath with alcoholic potash it is unchanged, unlike the isomeric dibenzaldiphenylhydrotetrazone which is converted by this treatment into β-benzilosazone by a remarkable intramolecular transformation. If the two osazones are treated with concentrated sulphuric acid, a wine-red colour is in each case produced. On adding water to the sulphuric acid solutions and subsequently distilling in steam, the α-osazone yielded benzil, benzaldehyd, and triphenylosotriazole (Auwers and V. Meyer, *Ber.*, xxi., 2806), while from the β-osazone (m. p. = 225°) the two latter substances were not produced. These facts, by analogy with the decomposition of the stereoisomeric benzildioximes, lead the authors to assign the syn-configuration to the α- and the anti-configuration to the β-osazone.

$$\begin{array}{ccc} C_6H_5\cdot C & \rule[0.5ex]{8em}{0.4pt} & C\cdot C_6H_5 \\ \| & & \| \\ \multicolumn{3}{c}{N\cdot NHC_6H_5C_6H_3\cdot HN\cdot N} \end{array}$$

α-Benzilosazone, m. p. = 208°.
Benzilsynosazone.



$$\begin{array}{rcl} C_6H_5\cdot C & - & C\rule[0.5ex]{2em}{0.4pt}C_6H_5 \\ \| & & \| \\ C_6H_5NH\cdot N & & N\cdot NHC_6H_5 \end{array}$$

β-Benzilosazone, m. p. 225°.
Benzilantiosazone.

This view is supported by the fact that the α-compound is the more easily oxidised. The two osazones show also different solubilities in various liquids.

The experiment of v. Pechmann (*loc. cit.*), who oxidised benzalphenylhydrazone with amyl nitrite in ethereal solution, was repeated, and from the mother-liquors the authors obtained a new substance, m. p. = 202°. Analysis showed it to be isomeric with the compounds before mentioned, but it differed from them in not being changed by alcoholic potash, or by heating with ethyl succinate; but, like the hydrotetrazone, it was reduced by phenylhydrazine to the original benzalphenylhydrazone. The constitution of this substance has not yet been determined with certainty.

71. "*Affinity of Weak Bases.*" By J. Walker, D.Sc., and E. Aston, B.Sc.

A method is described for estimating the strength of organic bases, such as aniline, from the rate at which equivalent solutions of their hydrochlorides invert cane-sugar at 60°. The results obtained are, as a rule, in agreement with those of previous experimenters. The same method applied to the nitrates of cadmium, zinc, lead, and aluminium gives the bases of these salts in the order of strength named.

72. "*Substitution-derivatives of Urea and Thiourea.*" By Augustus E. Dixon, M.D.

During the course of an investigation in which the author was engaged, it became necessary to verify the melting-points of certain urea and thiourea derivatives, and to obtain data regarding a number of compounds, hitherto unknown, belonging to the above classes. The following substances are described:—

Trimethylthiourea.—Thick, pointed prisms, very freely soluble in water, alcohol, and chloroform; desulphurised by silver, but not by alkaline lead solution, and melting at 87—88°.

Tribenzylthiourea forms silvery prisms, m. p. 114·5—115·5; insoluble in water, difficultly soluble in alcohol, freely in chloroform and benzene; decomposed on distillation.

Phenylmetatolylthiocarbamide, PhNH·CS·NHTo. — Vitreous prisms, insoluble in water, soluble in alcohol, ether, acetone, &c., and melting at 91—92°.

Orthoparaditolylthiocarbamide, $CS(NHTo)_2$. — Hard prisms, m. p. 172—173°, apparently undecomposed.

Phenylmetaxylylthiocarbamide.—White needles, melting at 125·5—126°; almost insoluble in water, sparingly soluble in cold alcohol, freely in chloroform.

Paratolyldibenzylthiourea, $ToN{:}C(SH)\cdot NBz_2$. — Short thick prisms or long slender needles (from alcohol) m. p. 145—146°; desulphurised by ammoniacal silver nitrate only on boiling, and not at all by alkaline lead solution.

Isobutylurea, spermaceti-like needles, becoming strongly electrical on friction; m. p. 140·5—141·5°; freely soluble in water and alcohol.

sec.-Butylurea.—Large flattened prisms, freely soluble in water, alcohol, and hot acetone; m. p. 169—170°.

Diisobutylurea, $CO(NH\textit{i}\text{-}Bu)_2$.—Prepared from the corresponding thiocarbamide and silver nitrate; it occurred in white needles, m. p. 135—136°.

Di-sec.-butylurea, $CO(NH\textit{s}\text{-}Bu)_2$, from sec.-butylurethane and sec.-butylamine; pearly flattened needles, melting at 137—138°.

ab-Methylphenylurea, MeNH·CO·NHPh.—Broad white prisms, moderately soluble in hot water, and melting at 150·5° and 151·5°, undecomposed.

ab-sec.-Butylphenylurea. — Large prisms (from hot alcohol); m. p. 155·5—156·5° without decomposition, insoluble in hot water.

ab-Phenylmetatolylurea and *ab-Phenylparatolylurea.*—White needles, melting at 173—174° and 212—213° respectively.

ab-Orthoparaditolylurea.—Flexible needles, melting at 263—264°.

ab-Ethylbenzylurea.—Long silky prisms, becoming very electrical on rubbing; m. p. 104—105°.

ab-Benzylorthotolylurea.—Small vitreous prisms (from alcohol); m. p. 188—188·5°; insoluble in water.

ab-Benzylmetatolylurea.—Flexible silvery needles, insoluble in water, freely soluble in hot spirit, and melting at 158·5—159°.

Methylphenylbenzylurea, MeNH·CO·NPhBz. — From the corresponding thiourea and silver nitrate, occurs in pearly white crystals of m. p. 107·5—108·5°, insoluble in water, very freely soluble in alcohol, ether, and chloroform.

ab-Allylphenylurea was found to melt at 114·5—115·5°, instead of 96—97°, as recorded by Maly.

The author suggests an addition to the nomenclature of thiourea-derivatives, with a view of rendering it more explicit.

73. "*Note on some Reactions of Ammonium Salts.*" By W. R. E. Hodgkinson and N. E. Bellairs, Lieut. R.A.

From the results of some experiments on metals and strong ammonia solution in presence of air (*Proc. Chem. Soc.*, 146, 9), the authors were led to examine the action of some metals on so-called ammonium salts. They chose for this purpose such salts of oxy-acids as may be melted in a comparatively dry state without appreciable decomposition.

So far they have only examined the nitrate and sulphate. These salts were dried and carefully melted, and the metal, in foil or thin sheet, introduced. The temperature in each experiment was maintained a few degrees above the melting-point of the salt.

Most of the experiments were quantitative.

Metallic copper acts immediately on the fused salts, ammonia gas and a little hydrogen being evolved. When the temperature is maintained below 160°, the residual product is a mixture of copper sulphate or nitrate with an excess of the ammonium salts; some water also escapes, and, in the case of ammonium sulphate, a small quantity of sulphite sublimes. Nickel and cobalt act in a similar manner, but more sublimate of sulphite is obtained, and the amount of hydrogen is very small. Mercury does not act so readily, but similar products are formed. The most easily managed reactions are those with silver and palladium. Silver dissolves most easily both in ammonium sulphate and nitrate; the amount of displaced ammonia is nearly equivalent to the silver dissolved as sulphate or nitrate. It is doubtful whether any hydrogen escapes. With ammonium sulphate much sulphite sublimes.

Palladium is very nearly as active as silver, and the main difference seems to be that a pallad-ammonium salt is produced, whilst the silver merely forms nitrate or sulphate.

The ammonium group seems to be displaced and broken up by metals at temperatures just below those at which the salts undergo re-solution if heated alone. In no case is the exact equivalent of ammonia to that of dissolved metal obtained. The metallic salt is always in excess, but silver dissolves more readily in fused ammonium sulphate than in sulphuric acid, probably owing to the easy fusibility of the mixed salts, silver sulphate and ammonium sulphate.

Research Fund.

A meeting of the Research Fund Committee will be held in June. Applications for grants, accompanied by full particulars, should be sent to the Secretaries before June 15th.

NOTICES OF BOOKS.

The Standard Dictionary of the English Language. London: Funk and Wagnall's Company, 44, Fleet Street. 1895.

The second and final volume of this excellent work has now come before us; the promise of the first volume is fully maintained in this, the completion.

There are many new and valuable features in this Dictionary; it has a vocabulary of more than 300,000 words, or 75,000 more than the most recent of its predecessors; in electricity alone something like 4000 new terms have been entered and described.

Its production has engaged the attention of no fewer than 237 editors and specialists, besides a staff of 500 readers, while the enormous sum of 960,000 dollars was expended before a single copy was ready for the market.

The remarks we made anent the first volume do not need repetition; it will suffice to say that the whole is a monument of industry and enterprise, and will assuredly rank as one of the best Dictionaries of the English and American languages.

At the end of this volume we find, in addition to the Dictionary proper, many useful adjuncts. There is a long list of many pages of words the spelling of which is doubtful or disputed; there is a glossary of foreign terms and quotations, with a curious list of obvious mistranslations by well-known authors; while it is also claimed that, for the first time in Dictionary-making, an attempt has been made to reduce the compounding of words to a scientific system. The new or phonetic spelling is still persisted in (to a certain extent), but we do not yet see any indication of its obtaining a firm footing, at least at this side of the Atlantic.

Chemical Laboratory Labels. Part 2, Third Edition. Compiled by W. H. Symons, F.I.C. London: Published by A. Gallenkamp and Co.

This part of the label book has been thoroughly revised and considerably extended since the previous edition, and planned, as far as possible to meet the requirements of the Science and Art Department; it now contains over 750 labels, and, in addition to the name of the substance, formulæ weights have in some instances been added. There is also a series of what may be described as special labels, *i. e.*, decinormal, centinormal, quintinormal, seminormal, &c., for standard solutions, besides several pages of blanks. The labels are all gummed, and clearly printed in bold type.

CORRESPONDENCE.

THE PREPARATION OF PHOSPHINE.

To the Editor of the Chemical News.

Sir,—The preparation of phosphine by the direct combination of hydrogen and amorphous phosphorus promised so many advantages for demonstration purposes that I repeated the experiment immediately after its publication. Like Professor McLeod, I found that on passing the gas through a wash-bottle containing water and then into the pneumatic trough, it merely fumed in contact with air. No variation in the temperature or in the rate of the current of hydrogen produced a gas spontaneously inflammable. A different result was obtained on omitting the wash-bottle and passing the gas directly into the pneumatic trough. So long as the current of hydrogen was slow only the fuming was observed, but as the rate of the current was increased flashes of light appeared amidst the fumes, and, finally, when the current of hydrogen had become fairly rapid, the gas became spontaneously inflammable.

Since reading Professor McLeod's letter to you, I have repeated the experiment, and have found that by passing the gas through a glass spiral kept cool by water the same effect is obtained as when the gas is passed through a wash-bottle containing water.—I am, &c.,

George Young.

Firth College, Sheffield.
May 27, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 20, May 20, 1895.

New Researches on the Thermic Relations among the Aldehyds, the Alcohols, and the Acids.—Prof. Berthelot and M. Rivals.—The authors have undertaken further experiments, multiplying the data by their extension to the salicylic, pyromucic, and camphenic series. From the table drawn up they conclude that the change of an aldehyd, properly so-called, into an alcohol by the fixation of H_2 evolves from 13 to 17 cal. in the fatty series, for the polyatomic alcohols studied as well as for the monoatomic alcohols. From this point of view camphor belongs to the fatty series. But we know that camphor by its easy conversion into cymene furnishes the connecting link between this series and the benzenic series. The change of an aldehyd into an acid by fixation of O liberates 60 to 68 cal., except for campholic aldehyd, which belongs to a group possessing special characters and yields only $+48{\cdot}8$. If we consider the oxidation with reference to the alcohols in its two successive degrees, formation of aldehyds and formation of acids, we find that the first degree liberates in general less heat than the second.

Existence of Phosphorus in Oysters in a Notable Proportion.—A. Chatin and A. Müntz.—The authors, in their recent analyses of oysters, have found an unexpected proportion of calcium phosphate, and have observed that this proportion is much greater in the Portuguese oyster (*Gryphæa angulata*) than the French oyster (*Ostrea edulis*). The shells of the Portuguese oyster contain 0·089 per cent, whilst those of the French oyster contain only 0·038. The same superiority was observed in the former when the two kinds had been raised for a year in the same beds at Sable-d'Olonne. The flesh in 100 parts of dry organic matter yielded, in the French species, 1·836 of phosphoric acid, and in that of Portugal 2·052.

Classification of the Chemical Elements.—Lecoq de Boisbaudran.—(See p. 271).

Spectral Analysis of the Gases given off by various Minerals.—Prof. Norman Lockyer.—On heating minerals *in vacuo* and examining the gas obtained by this process I have already found about 60 spectral lines which are, I believe, new in terrestrial chemistry. Among these minerals was uraninite, from which Prof. Ramsay has obtained a gas showing in the yellow the line which in 1869 I referred to the hypothetical element helium. Hitherto I have examined 18 minerals. The spectra show that several gases are here in question. The author gives tables of the approximate λ of the lines already photographed and remarkable coincidences of these wavelengths with those of the unknown lines in the white stars of Orion and in the chromosphere of the sun.

Hydrogenising Properties of the Sodium Alcoholates at High Temperatures.—A. Haller and J. Minguin.—The authors have extended the study of this action to various bodies having a ketonic function, especially to desoxybenzoine, benzophenone, and anthraquinone.

Comparison between the Spectra of the Gas of Clèveite and that of the Solar Atmosphere.—H. Deslandres.—This memoir will be inserted in full.

Isomeric Transformations of the Salts of Mercury.—Raoul Varet.—A table of the heat disengaged on the reciprocal metamorphoses of the salts of mercury in their isomeric states.

Action of Nitrogen Peroxide on the Haloid Salts of Antimony.—V. Thomas. — Not suitable for useful abstraction.

Formation Heats of Benzoyl and Toluyl Chlorides.—Paul Rivals.—The formation heat of liquid benzene (−4·1 cal.) and of solid benzoic acid (+94·2 cal.) gives a difference of +98·3 cal.

A Study of Senecionine and Senecine.—A. Grandval and H. Lajoux.—The authors have operated upon *Senecio vulgaris.* Senecionine has the composition $C_{18}H_{26}NO_6$. It does not display striking reactions. Senecine is incomparably more bitter than senecionine. Its analysis is not given. With sulphuric acid it gives a yellowish colouration, inclining to brown; with nitric acid a reddish violet colour and a deep violet precipitate. With sulpho-vanadic acid a violet-brown colour.

On Benzene-sulpho-orthotoluidine and some of its Deeivatives.—Ch. Rabaut.—The author points out the great resistance of benzene-sulpho-orthotoluidine to oxidation, and its great stability in presence of hot dilute acids, notwithstanding its character as an amide.

Analysis of the Bones of a Mummy.—M. Thezard'—The tibia of an adult, white, very brittle, and of uncertain date. Some of the tombs from which it has been procured date back to 4500 B.C., and others only to 665 to 527 B.C., or even to the epoch of the Ptolemies, 306—30 B.C. Its composition is:—

Moisture	7·900
Organic matters (nitrogenous)	19·769
Fatty matter	0·850
Other organic matter	3·412
Tricalcic phosphate	50·940
Magnesium phosphate ($2MgO,PO_5$)	2·095
Calcium carbonate	10·365
Potassium nitrate	0·270
Sodium nitrate	0·644
Sodium chloride	1·338
Sodium sulphate	0·469
Iron oxide	0·240
Alumina	0·534
Silica	0·800
Fluorine	traces
Not determined	0·374
	100·000

On a Leucomaine obtained from the Urine of a Patient suffering from Angina pectoris.—Dr. A. B. Griffiths and C. Massey.—This base is white and crystalline, soluble in water; reaction slightly alkaline. It forms a crystalline hydrochlorate, chloroplatinate, and chloraurate. It gives a yellowish precipitate with phosphotungstic acid, a yellow with phosphomolybdic acid, a red with tannic acid, and a greenish with silver nitrate. With mercuric chloride it gives a green precipitate, and with Nessler's reagent a brown precipitate. Its composition agrees with the formula $C_{16}H_9NO_4$. It is very poisonous, producing fever and death in two hours. It is not present in normal urine.

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.

Tests for Morphine in Urea.—(Reply to A. R. P.).—An article on the "Recovery of Absorbed Morphine from the Urine, the Blood, and the Tissues," by Dr. T. G. Wormley, appeared in the Chemical News for August 8, 1890 vol. lxii., p. 65).—T. G. W.

Deodorising Petroleum.—Will some correspondent kindly inform me if there is an inexpensive way of removing the odour from petroleum oil. I want to mix it with another substance, but the smell the oil imparts would make it most disagreeable.—C. R.

MEETINGS FOR THE WEEK.

Tuesday, 11th.—Medical and Chirurgical, 8.30.
— Photographic, 8.
Thursday, 13th.—Royal, 4 30.
— Royal Society Club, 6.30.
— Mathematical, 8.
Friday, 14th.—Physical, 5. "The Measurement of Cyclically varying Temperature," by H. F. Burs all. "The Thermal Constants of the Elements," by N. F. Deere, "An Electromagnetic Effect," by F. W. Bowden.
— Astronomical, 8.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1855.

ON THE DENSITY OF HELIUM.[*]

By M. CLÈVE.

M. Langlet, who is occupied in the University of Upsala on the study of helium, has lately determined its density. The gas extracted from clèveite was freed from hydrogen by passing it over oxide of copper heated to redness, and from nitrogen by means of metallic magnesium. It did not contain argon. Its density was found to be 0·139 (air = 1), or 2·02 (hydrogen = 1). This number is decidedly lower than the density found by Professor Ramsay. We are now occupied in determining the specific heat of the gas.

[Some weeks ago Professor Ramsay told me that he had obtained helium, pumped off at a red heat from brüggerite, of as low a density as 2·18.—*Ed.* C. N.]

SOLAR AND TERRESTRIAL HELIUM.

The Editor has the writer's permission to print the following private letter to himself:—

Runge having stated (*Nature*, June 6, 1895, p. 188) that the yellow line of the gas which he obtained from clèveite is double, and that neither of the component lines has exactly the place of the helium line, which falls between them, this new gas, as Runge points out, cannot be helium, unless the bright line D_3 in the sun is similarly double.

Though I had no doubt from former observations of my own, as well as from the measures of the line by Jewell for the Rowland tables, that the solar line is single, I have now examined the line again with a 4-inch Rowland grating of 14,438 to the inch, using the third order of spectrum, and a magnifying power of 29 diameters.

At the sun's limb the helium line appeared, as it usually does of some breadth, but at favourable moments I saw the line, as also did Mrs. Huggins, fine off to a very fine single point.

There can be no doubt that the helium line in the sun is not double, as Runge states the new gas line to be.

In this connection I may mention observations of Bélopolsky (*Mem. Società Spett. Ital.*, May, 1894), who saw occasionally a pair of dark terrestrial lines come in at the sides of the bright helium line.

The wave-lengths of these lines agree pretty well with Runge's measures. May it be that the clèveite gas is the stuff giving rise to these terrestrial lines? A similar suggestion was made to me some weeks ago by Dr. Blumbach, before Runge had shown the new gas line to be double.

Bélopolsky's measures are given in the Potsdam scale, which differs from that of Rowland by less than one unit in the first decimal place.

	Runge's measures.		Bélopolsky's measures.
	5875·883		5875·8
(Helium..	5875·982)	(Helium..	5876·0)
	5876·206		5876·5 (double)

The measures for D_1 and D_2 are—

Potsdam.	Rowland.
5896·25	5896·156
5890·23	5890·188

William Huggins.

90, Upper Tulse Hill, S.W.,
June 10, 1895.

TERRESTRIAL HELIUM (?).

By Professor C. RUNGE.

The following communication appeared in last week's *Nature*:—

Prof. Paschen and I have lately made a careful determination of the wave-length of the strong yellow line emitted by clèveite when heated in a Plücker tube. We owe the mineral to the kindness of Prof. Rinne. My large Rowland concave grating, of 6·5 metre radius, clearly shows the yellow line to be double. Its less refrangible component is much weaker, but comes out quite bright when the stronger one is brilliant. We photographed the two lines together with the second order of the spark spectrum of iron. There are a number of iron lines on each side that are included in Rowland's list of standard wave-lengths (*Phil. Mag.*, July, 1893). From these we interpolated the wave-lenths of the yellow lines by micrometric measurement. Three different plates taken on different days gave us—

Strong component.		Weak component.
5875·894	.. ..	5876·216
5875·874	.. ..	5876·206
5875·880	.. ..	5876·196
Mean 5875·883		Mean 5876·206

We think an error of more than 0·025 very improbable.

Now Rowland's determination of D_3 (*Phil. Mag.*, July, 1893) is—

5875·982,

the result of three series of measurements which he believes to be accurate to 0·02.

The difference between this value and the wave-length of the strong component is much too large to be accounted for by an error of observation.

We do not therefore agree with the conclusion, drawn by Mr. Crookes, that the unknown element helium causing the line D_3 to appear in the solar spectrum is identical with the gas in clèveite, *unless D_3 is shown to be double.* Perhaps Prof. Rowland will tell us if this might have escaped his notice. From his note on D_3 in *Phil. Mag.*, July, 1893, it appears that D_3 cannot have been so wide as to include both lines, because he would then not have considered his determination accurate to 0·02. As for dispersion, one may see in his table of solar spectrum wave-lengths that he has frequently measured three and even four lines in an interval as large as the one between the components.

Hanover Techn. Hochschule, May 16.

CERIUM,

By BOHUSLAV BRAUNER, Ph.D., F.C.S.,
Late Berkeley Fellow of Owens College.

During the last seventeen years I have been engaged in the investigation of the rare earth-metals of the cerium group, and the results obtained by me were published in the years 1881, 1882, 1883, 1885, 1888, and 1891, in the *Journal of the Chemical Society*, in the *Proceedings* and the *Transactions of the Vienna Academy*, the *Comptes Rendus*, and the *Berichte*.

One of the papers was devoted to the study of the atomic weight of cerium. It was shown in that paper most distinctly that ordinary cerium is a mixture of two substances, the real cerium with the atomic weight of 140·2 giving a nearly white oxide, and a substance giving an oxide of a peculiar *flesh-colour mixed with orange*, with a higher atomic weight. The last was found to rise to 142·65, and even to 145·72. Fractions showing this high atomic weight were obtained on precipitating the mother-liquors, from which the sulphate of the ordinary

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[*] A letter from M. Clève to M. Berthelot, in the *Comptes Rendus* for June 4th, 1895 (vol. cxx., p. 1212).

cerium has crystallised out, by alcohol. Knowing the difficulty of my position, I was too modest to declare the substance as the compound of a new element, and only concluded that "under certain conditions 'cerium' may consist of a mixture, The nature of this admixture must be ascertained by further experiments."

Schützenberger has lately (*Comptes Rendus*, cxx., 633 and 962, and Chemical News, lxxi, p. 188) published two papers on the same subject. He obtained cerium by Debray's method, and it was split up exactly by the same method which was used and described by me ten years ago into "cerium (1)," with a nearly white oxide and the atomic weight 139·5, and "cerium (2)," with an oxide "rouge rosé ou brun rose clair." The synthesis of the sulphate gives numbers varying between 142·4 and 143·3.

I am very sorry to remark that not the slightest reference was made here to my work, though the method used and many of the results obtained by the illustrious French chemist are absolutely the same as those described by me in English and German.

The novelty of Schützenberger's research consists in using Debray's method, and in establishing the fact that other methods of analysis give for the atomic weight of "cerium (2)" results varying between 136 and 138·75.

In order not to lose the priority of the above discovery and the right of continuing my research, I may be allowed to give a short account of the results obtained by me during the last years.

I devoted first my attention to the study of the salt, which was considered formerly as a sulphate of the trioxide Ce_2O_3 as long as cerium was regarded as divalent Ce=94. (With Ce=141 this oxide becomes Ce_4O_9.) The old formula was—

$$2CeSO_4.Ce_2(SO_4)_3+18H_2O.$$

Mendeleeff in 1873, on proposing the new atomic weight of cerium (*Ann.*, clxviii., p. 45), regarded the salt as a double sulphate of trivalent cerium with tetravalent cerium:—$Ce_2O_3.3SO_3+Ce_2O_4.4SO_3+24H_2O$.

I have proved by the following methods that the salt possesses really the composition assumed by Mendeleeff:—

1. By numerous analyses of the salt. By this method alone, unfortunately, no constant results could be obtained, for the salt, crystallising only from a solution which contains much free sulphuric acid (*i.e.*, 25 per cent H_2SO_4!), always contains a considerable excess of this acid, probably mechanically included.

2. By synthesis of the salt from the single constituents, $Ce_2(SO_4)_3.8H_2O$ and $Ce_2(SO_4)_4.8H_2O$.

3. Trivalent cerium was replaced by other trivalent earth-metals and their sulphates, combined with the tetrad ceric sulphate. In this way a *new series of double sulphates* of trioxides with those of cerium tetroxide was obtained, and, as they show a great similarity of form with Mendeleeff's salt, they are being crystallographically investigated by Prof. Urba. The new lanthano-ceric salt is an example, and its analysis agrees, though not quite well, with the formula—

$$La_2O_3.3SO_3+Ce_2O_4.4SO_3+24H_2O.$$

4. The synthesis and analysis of the salt *alone* not proving sufficient for the establishment of the formula, the mother-liquors from which the salt has separated were analysed completely, and found to contain 26·18 per cent of sulphuric acid, only partly combined to cerium and lanthanum. The molecular proportion of its constituents is, in round numbers, $1R_4O_7 : 23SO_3 : 333H_2O$, and it is easily understood that, by an inclusion of such a highly acid mother-liquor, the composition of the salt is most considerably altered. After applying a correction for the included mother-liquor, the formula of the above salt becomes $La_2O_3.3SO_3+Ce_2O_4.4SO_3+18H_2O$.

This salt throws some light on the real composition of the analogous ceroso-ceric sulphate which was at first regarded by me as an acid salt. But this view was given up, as the salt rarely contains so much free sulphuric as to correspond with the composition of an *acid sulphate*.

Some work was devoted also to the preparation of the tetrachloride of cerium and its double salts, corresponding with the tetrafluoride and its double salts discovered by me (1882); the result was obtained that ceric hydrate exists in two modifications. The one is insoluble in cold hydrochloric acid, the other dissolves in hydrochloric acid; but the brownish-yellow solution of the tetrachloride obtained decomposes even at the temperature of −18° with evolution of chlorine.

I have devoted much time to attempts to split up cerium into its constituents, and succeeded in doing so, more or less completely, by the following experiments:—

1. By fractional solution of ceric oxide in sulphuric acid. The remaining portions were absolutely insoluble in boiling concentrated sulphuric acid, and after being brought into solution either by fusion with $KHSO_4$ or by boiling with hydrochloric acid and potassium iodide, the oxalate gave on ignition a rose-brown (dark salmon-coloured) oxide of an element, which I would design provisionally as "meta-cerium."

2. By partial reduction of ceric oxide in hydrogen, and extraction of the products obtained.

3. By fractional precipitation with oxalic acid.

4. By fractional crystallisation of the sulphate, and precipitation of the mother-liquor by alcohol. (This method was used and described by me ten years ago.)

5. By fractional crystallisation of the *ceric*-ammonium nitrate.

6. By fractional crystallisation of the *cerous*-ammonium nitrate. (This is Mendeleeff's method, *l.c.*, and was accepted by Auer von Welsbach without reference to Mendeleeff.)

7. The new earth is accumulated in the mother-liquor after precipitation of cerium as basic nitrate or sulphate, and can be obtained from them by combining Debray's method with one of the above methods.

I have also examined the spark spectra of the different fractions of cerium, and I find that some lines are common to cerium and to meta-cerium, whereas other lines are characteristic for each of them.

Not being satisfied with the results of my former method of atomic weight determination of cerium, by the conversion of the anydrous cerous sulphate into ceric oxide, the results of which varied between 140·03 and 140·43, on account of the slightly varying composition of ceric oxide, I made a new series of determinations based on the analysis of the normal *oxalate* by the method of Gibbs (*Proc. Amer. Acad.*, xxviii., 260—279). In order to exclude the error due to the varying composition of the ceric oxide, the quantity of "active" oxygen contained in it over and above Ce_2O_3 was most carefully determined by Bunsen's method (*Ann.*, cv., 40), and care was taken to introduce a correction due to the liberation of a trace of iodine during the action of 10 c.c. hydrochloric acid upon 1 gr. KI, as found by a blank experiment.

The determinations may be checked by determining the amount of water contained in the air-dry oxalate and the oxalate dried over phosphorus pentoxide, and by the synthesis of the sulphate from the oxalate.

The determination of the oxalic acid radical was done by *old* potassium permanganate of an invariable standard. This last mode of determination requires great practice, because, as soon as all oxalic acid is oxidised, the trivalent cerium present begins to be oxidised to the tetravalent state, but not sooner, as oxalic acid is oxidised by ceric sulphate, a reaction which can be used for the volumetric determination of ceric salts. The details of one of the determinations show the applicabilty of the method:—

100 parts of the pure cerous oxalate were found to contain (*a*) 29·506 p.c. C_2O_3, (*b*) 29·503 p.c. C_2O_3, and (*c*) 46·934 p.c. of the dioxide. This contains surplus oxygen, (*d*) 2·155 p.c. (corrected), and (*e*) 2·235 p.c. (uncorrected). The atomic weight of cerium, calculated from (*a*), (*b*), and (*c*), is Ce=139·91; that from (*a*), (*b*), (*c*), and (*d*), Ce=140·01;

from (*a*), (*b*), (*c*), and (*e*), Ce = 139·72. The third number shows that a correction of the above kind must be introduced; the first and the second methods of calculation give numbers differing only slightly from each other, and the method of analysis is entirely free from the great variations inherent to the methods used by Schützenberger. It has been shown by many chemists, and especially by Th. W. Richards in his wonderfully exact researches, that the method of determining sulphuric acid as barium sulphate (not to say in the presence of alkalies, as done by Schützenberger!) is so vicious as to prove *absolutely inapplicable* for the determination of atomic weights, and very little confidence can therefore be placed in the number Ce = 139·5, found by this method by Schützenberger.

I prefer the number Ce = 140·01 obtained by me by the above combined method, after applying the said correction, and regard it as an exact determination of the atomic weight of cerium.

The fact that potassium permanganate oxidises colourless *cerous* salts to yellow *ceric* salt was used by me for the volumetric determination of cerium. In an acid solution the end of the reaction cannot be seen, on account of the deep yellow colour of the ceric salt formed. The method gives, however, excellent results in alkaline solution:—

$$3Ce_2O_3+2KMnO_4+H_2O+Aq= \\ =2KOH+2MnO_2+3Ce_2O_4+Aq.$$

The excess of permanganate used is determined in the filtrate, after removal of the hydrated oxides formed by filtration through a Gooch.* This method has proved invaluable for the determination of trivalent cerium in the presence of tetravalent cerium, and of cerium in any form (tetravalent cerium may be first reduced by sulphurous acid) in the presence of other non-oxidisable earths. The results obtained for the "atomic numbers" of "meta-cerium" give invariably higher numbers in contradistinction to the results obtained by Schützenberger.

I think that these higher numbers are correct also for the theoretical reason that there is no room in the periodic system for a cerium-like element with a lower atomic weight than cerium. On the other hand, many rare earth-metals may exist with higher atomic weights than 140. The most interesting question—whether "meta-cerium" is not Mendeleeff's "ekacerium" of 180?—will have to be answered by further investigation.

Before concluding this preliminary notice some theoretical remarks may be allowed. The question arises—Where is there a place in the periodic system for the numberless rare earth-metals (true chemical asteroïds) the atomic weight of which varies between 140 and 170? The following suggestion may throw some light on that question:—

On considering the position of the rare-earth elements in the periodic system, we arrive at the following conclusion:—"*The valency of the rare-earth elements increases with increasing atomic weight.*"

Beryllium, Be = 9, is undoubtedly a *divalent* rare-earth element, with the oxide RO, as was shown by the author in 1878, 1881, and 1882.

Then come the *trivalent* elements: scandium, Sc = 44; yttrium, Y = 89; lanthanum, La = 138; and ytterbium, Yb = 173, with the oxides, R_2O_3.

Cerium, Ce = 140, forms a transition to the tetravalent earth elements, being both *trivalent* and *tetravalent*, with the oxides R_2O_3 and R_2O_4.

Thorium, Th = 232, is only *tetravalent* with the oxide R_2O_4, though a lower oxide, Th_2O_3, may exist, corresponding to the lower oxides of niobium and tantalum.

At the present limit of the periodic system and outside it rare-earth elements may be expected, possessing the oxides R_2O_5, R_2O_6, and perhaps even R_2O_7 and R_2O_8, with distinct basic properties. Very probably the atomic weight of either neodymium (R''' = 140·5) or praseodymium (R''' = 143·5) will be 235 and the oxide R_2O_5, or 282 and the oxide R_2O_6 (a true Neptune of the periodic system), for only one of both constituents of the old didymium, more probably praseodymium, yielding salts of the higher oxide, which seems to be as unstable as is $CeCl_4$ (see above), will find its place in the eighth series next to cerium.

The association of the rare-earth minerals with argon and helium, and their rarity on the surface of the earth, indicate that we have to do here with the heaviest atoms, the normal geological position of which is in the interior of our earth.

Being obliged to do all this and other difficult work myself alone, without the slightest assistance or help, my time does not allow me to go on so quickly with my work as I would like it; and had it not been for the fact that Schützenberger has repeated a great part of my work without making any reference to it, I should have delayed the publication of the results arrived at years ago until the character of the new constituent of cerium could have been described more definitely.

Bohemian University, Prague,
May 28, 1895.

NOTE ON THE ESTIMATION OF TOTAL ALKALI IN SOAP.

By J. A. WILSON.

In titrating soap solutions by standard acid, especially in the case of soap prepared from solid fats, as tallow, palm oil, &c., the end of the neutralisation when using methyl orange as indicator, at a temperature of, say, 25° C., is not very definite, the pinkish tint gradually disappearing on violent stirring. This is due to traces of the soap solution becoming enveloped in the precipitated fatty acids, and then not easily being acted upon by the acid employed in titration.

The error is great enough to render determination of the free alkali (by difference) unreliable, and I have now given up direct titration.

The following examples illustrate the above remarks:—

Sample No.	Percentage of Na_2O. Direct.	Indirect.
63.	6·71	6·94
35.	5·43	5·54
98.	8·28	8·39

Newchurch, Rossendale,
May 27, 1895.

MELTING-POINT OF THE ELEMENTS AS A CLUE TO THEIR GENESIS.

By C. T. BLANSHARD, M.A.

A. Baeyer was the first to observe (*Ber.*, x., 1286) that in several series of organic compounds the melting-points are alternately high and low with each increment of the grouping CH_2. He further observed that compounds containing an even number of carbon atoms have high melting-points, whilst those with an uneven number have comparatively low melting-points. Thus, to take as an example the fatty acids, as, all being tolerably well known bodies, these afford plenty of data, we have the following figures from the most recent sources. I quote from H. Landolt and R. Börnstein, "Physikalische-Chemische Tabellen," Berlin, 1894.

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* This method may be used for the determination of a large number of elements giving lower and higher oxides.

Compounds.		Formula.	High m.p. °	Low m.p. °
Formic acid	.. ..	CH_2O_2		8·6
Acetic acid ..	.. ..	$C_2H_4O_2$	16·75	
Propionic acid	.. ..	$C_3H_6O_2$		−24
Butyric acid	.. ..	$C_4H_8O_2$	−4	
Valeric acid	.. ..	$C_5H_{10}O_2$		below −16
Caproic acid	.. ..	$C_6H_{12}O_2$	−1·5	
Œnanthylic acid	..	$C_7H_{14}O_2$		−10·5
Caprylic acid	.. ..	$C_8H_{16}O_2$	16·5	
Pelargonic acid ..	..	$C_9H_{18}O_2$		12·5
Capric acid ..	.. ..	$C_{10}H_{20}O_2$	29·5	

The acids considered are the normal ones.

If the elements are arranged in their natural groups, and the melting-points compared, no such alternation is found. But an arrangement of the elements in order of atomic weight, that is to say in periodic series, reveals such alternations of high and low melting-points. The melting-points given are those to be found in an article in the January number of the *Phil. Mag.* for this year ([5], xxxix., p. 106), with the substitution of the latest values for Cu, Ag, Mg, Zn, Al, Sb, namely those of C. T. Heycock and F. H. Neville (*C. J.*, 387, p. 186, Feb., 1895), and the addition of Olszewski's value for N. The figures here are given in round numbers. In the article in the *Phil. Mag.* referred to, the exact figures together with the authorities will be found; but it will suffice here to give fewer, and those in simpler form.

I have suggested the melting-points −200° for O, and −182° for F, for the following reasons.

Prof. Dewar (Chem. News (lxxi., p. 199) finds that air remains a half solidified jelly at −210°. Now nitrogen solidifies at −214°; it would therefore seem that the melting-point of oxygen is higher than this. The value for nitrogen is Olszewski's. With regard to fluorine the melting-point of I is 114°, that of Br 121° less than this, that of Cl 95° less than that of Br. We should therefore expect the melting-point of F to be 80° (the geometric mean) less than of Cl, viz., −182°. The other queried values have all been ascertained by able authorities, but not in definite figures.

Series 1.

Element.	°M.p.
Li	180
Be	900
B	2700 ?
C	3000 ?
N	−214
O	−200 ?
F	−182 ?

Series 2.

Element.	°M.p.
Na	96
Mg	633
Al	654
Si	1200 ?
P	44
S	114
Cl	−102

Series 3.

Element.	°M.p.
K	62
Ca	—
Sc	—
Ti	2500 ?
V	—
Cr	2200 ?
Mn	2000 ?

Series 4.

Element.	°M.p.
Cu	1080
Zn	419
Ga	30
Gl	900 ?
As	200 ?
Se	250
Br	−7

Series 5.

Element.	°M.p.
Rb	38
Sr	—
Y	—
Zr	—
Nb	—
Mo	—
*	—

Series 6.

Element.	°M.p.
Ag	960
Cd	321
In	176
Sn	233
Sb	629
Te	455
I	114

Series 5 and the series above the 6th do not yield any comparable results, the melting-points being very defective. Series 1 shows no alternation, but Series 2, beginning with the third member Al, probably Series 3, Series 4, beginning with the second member Zn, and Series 6, beginning with the second member Cd, all show alternation of high and low melting-points, the only exception being Sb.

The above data may be considered to establish the two following laws:—

1. With elements of both low atomicity and low atomic weight melting-point varies directly as atomic weight.
2. In the higher periodic series of elements the melting-points are alternately high and low, with increase of atomic weight.

That is to say, in all the elements but those which from their low atomic weights may reasonably be regarded as the very simplest, a relationship maintains which has been observed in numerous series of organic substances.

It is reasonable, therefore, to suppose that such elements with higher atomic weights are in reality substances of a higher grade than the others, in that they resemble such highly evolved bodies as carbon compounds, at any rate in respect of melting-point.

There is another way, however, in which a parallel can be drawn, and that is in respect of specific volume. This I must reserve for a future article.

THE ACTION OF HEAT UPON ETHYLENE.*

II.

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

(Continued from p. 273).

Table III.

Temperature, 900° C. Rate of Flow, 40 c.c.

Length of tube heated.	1 inch.		6 inches.		18 inches.	
Volume of gas—						
Before heating ..	870		1050		1000	
After heating ..	790		985		980	
Analysis of Gaseous Products.						
Carbon dioxide ..	0·75		0·50		0·25	
Oxygen	0·50		0·75		0·50	
Unsaturated hydrocarbons	50·80		35·75		9·75	
Carbon monoxide	1·50		1·00		1·50	
Saturated hydrocarbs. by absorp.	11·22	27·67	11·25	41·75	10·00	56·50
Do. by explos.	16·45		30·50		46·50	
Hydrogen	14·50		16·65		28·00	
Nitrogen	4·28		3·60		4·00	

Calculating the percentage for the change in volume, we obtain the following figures:—

Length of tube heated.	1 inch.	6 inches.	18 inches.
Unsaturated hydrocarbons	46·12	33·53	9·55
Saturated hydrocarbons	25·12	39·16	55·37
Hydrogen	13·16	15·61	27·44

The original gas contained 96·7 per cent of ethylene, so that the percentages of unsaturated hydrocarbons decomposed are:—

Length of tube heated.	1 inch.	6 inches.	18 inches.
	50·58	63·17	87·15

On collecting these results in one table—

Percentage of Ethylene decomposed.

Length of tube heated.	1 inch.	6 inches.	18 inches.
5 c.c.	80·10	85·48	93·76
15 c.c.	70·83	79·42	90·31
40 c.c.	50·58	63·17	87·15

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* A Paper read before the Royal Society.

The first thing that strikes one is the enormous amount of decomposition which takes place in the first inch of flow through the heated tube, and the small effect which an increase in the length of the heated surface has upon the further decomposition of the unsaturated hydrocarbons.

This result might be caused by the methane and hydrogen formed during the decomposition diluting the remaining ethylene, and so rehdering the decomposition more difficult; it may also arise from secondary actions taking place amongst the primary products, and again forming ethylene, or it may be due to both these causes acting together.

In order to trace the effect of dilution, a series of experiments was made in which ethylene, diluted with hydrogen, was passed through 6 inches of the same tube as was used in the previous experiments, heated to the same temperature, and under precisely similar conditions.

The store holder of ethylene used for making the mixture contained a gas which gave on analysis—

Ethylene	97·85
Nitrogen	2·00
Oxygen	0·15

Table IV.

Influence of Dilution in Checking Decomposition of Ethylene.

Length of tube heated, 6 inches. Rate of Flow, 10 c.c. per minute. Temperature, 900° C.

Percentage of hydrogen	nil		10·0		25	
Do. of ethylene ..	98·7		90·0		75	
Volume of gas—						
Before heating..	100·0		100·0		100	
After heating ..	81·3		69·5		69	
Analysis of Products of Decomposition.						
Carbon dioxide ..	1·00		0·75		0·50	
Oxygen	0·50		0·25		0·25	
*Unsaturated hydrocarbons ..	32·52		31·00		29·00	
Carbon monoxide	1·00		1·25		1·00	
Saturated hydrocarbs. by absorp.	17·75	50·25	14·50	50·75	14·50	48·45
Do. by explos.	32·50		36·25		33·95	
Hydrogen	12·62		14·25		18·50	
Nitrogen	2·11		1·75		2·30	
*Containing acetylene	1·06		0·52		0·73	

Percentage of hydrogen	50		75		95	
Do. of ethylene ..	50		25		5	
Volume of gas—						
Before heating..	100		100		100	
After heating ..	64		85		100	
Analysis of Products of Decomposition.						
Carbon dioxide ..	1·25		0·50		—	
Oxygen	—		0·15		—	
*Unsaturated hydrocarbons ..	22·25		11·10		2·00	
Carbon monoxide	1·25		1·00		0·50	
Saturated hydrocarbs. by absorp.	8·50	36·00	5·50	15·80	0·75	4·85
Do. by explos.	27·50		10·30		4·10	
Hydrogen	37·15		68·45		89·15	
Nitrogen	2·10		3·00		3·50	
*Containing acetylene	0·32		0·15		trace	

On calculating these percentages for the change in volume, we obtain the following results:—

	I.	II.	III.	IV.	V.	VI.
Unsat. hydrocarbons ..	25·58	21·18	19·50	14·04	9·30	2·00
Saturated do.	40·85	35·27	33·43	23·04	13·43	4·85

The ethylene taken only contained 97·85 per cent of the hydrocarbon, hence—

	I.	II.	III.	IV.	V.	VI.
Unsat. hydrocarbs. originally present	97·85	88·02	73·35	48·90	24·45	4·89
Do. do. present after heating ..	25·58	21·18	19·50	14·04	9·30	2·00
Do. do. decomposed	72·27	66·84	53·85	34·88	15·15	2·89

and calculating this to percentage of total ethylene decomposed—

I.	II.	III.	IV.	V.	VI.
73·86	75·94	73·24	71·30	61·96	59·10

which shows that dilution has practically no effect in retarding the decomposition until 75 per cent of diluent is present, and also clearly points to its being radiant heat, and not contact with the heated sides of the tube, which is responsible for the largest proportion of the decomposition, as had contact been the active factor, dilution, by reducing the number of impacts of the hydrocarbon molecules with the heated surface, would have shown a considerable decrease in decomposition.

(To be continued.)

THE ADULTERATION ACTS.

There are several matters of more than ordinary interest touched upon by Mr. Frank L. Teed, public analyst to the parish of Camberwell, in the quarterly report which he has just presented to the Vestry. "Two rather curious cases," Mr. Teed states, "have recently been decided in connection with the Acts governing the Sale of Food and Drugs. In one a vendor was summoned for, and after much legal argument convicted of, the rare offence of selling a drug, diluted acetic acid, of greater strength than laid down in the British Pharmacopœia. This offence at first sight may not seem important, but when it is considered that medical men in prescribing medicines have to rely on the pharmacist supplying drugs as prescribed, and that if the pharmacist supplies a stronger drug serious consequences may arise, its importance becomes more apparent. The same offence is punishable under the Pharmacy Act with a penalty of £5, but I understand that the Secretary to the Pharmaceutical Society is the only man who can proceed under this Act. The other case has perhaps more important consequences, and that is a decision of the High Court that penalties under the Margarine Act, 1887, are to go to the prosecuting authority. It is a question of some importance whether former penalties inflicted under this Act are not still recoverable by the Vestry."

With respect to the inactivity of the Vestry in carrying into effect the Adulteration Acts, Mr. Teed remarks:—"I have from time to time felt it my duty to bring to your notice that fewer samples were taken in Camberwell in proportion to the population than in the rest of London taken as a whole. The Annual Report of the Local Government Board for 1893-94, the latest report out, states 'In London one sample was obtained for every 530 persons.' To bring Camberwell into line with the rest of London the number of samples must be more than doubled. I have placed these figures before you, as they have a direct bearing on the administration of the three Acts designed to suppress adulteration. While on the subject of the above Report I may mention that the action of this Vestry in testing the genuineness of milk as it arrives from the country is favourably commented upon. The importance of this branch of the crusade against adulteration can scarcely be over-estimated, as, in addition to other benefits, it not only protects the consuming public but also the honest retailer, struggling for existence in the whirl of the conflicting interests of mercantile competition. This Report also alludes to the high percentage of adulterated milk samples purchased on Sundays, and to the diluted condition of milk supplied to some public institutions. The minimum number of samples was not reached this quarter, only 17 samples as against 50 having been taken. I can only revive a former suggestion of mine, that an Inspector should be especially allotted to this work, not necessarily for his whole time, but the collection of the requisite number of samples to be his primary duty."

CONTRIBUTION TO THE HISTORY OF THE EARTHS OF CERITE.*

By P. SCHUTZENBERGER.

After the elimination of the cerium by melting the nitrates between 320° and 330° along with 8 to 10 parts of saltpetre, the saline mass separated from CeO_2 by solution in water, filtration, and evaporation to dryness, is fused again, and kept between 350° and 360° up to tranquil fusion. Nitrous gas is no longer evolved, except in very small quantity.

The object of this operation is the removal of the last traces of cerium. We dissolve, filter, and evaporate to dryness in order to proceed with the residue to fractionated separations by heating to higher temperatures.

Five successive fractions have thus been obtained between 400° and 420°, and three others between 430° and 460°.

The subnitrates, insoluble in water, separated each time, have been converted into oxalates, and then into oxides very free from alkali.

The oxides were then heated to bright redness, and for each fraction the atomic weight was determined by converting it into sulphate. As a control we returned to oxide by igniting the anhydrous sulphate at bright redness. These operations do not present the same difficulties as those with cerium, the oxides being always brought back by ignition to the lesser degree of oxidation, M_2O_3.

The method followed is an extension of the Debray process to the separation of lanthanum and didymium.

Making use of the names generally accepted, we shall call—

1. *Earths of the ceric group;* all the earths which form double potassium sulphates, insoluble in a saturated solution of potassium sulphate.
2. *Cerium oxides:* those of the above earths which are capable of being converted into bioxides CeO_2, the colourless salts of which furnish no absorption bands.
3. *Oxides of didymium;* those of the earths which yield salts more or less rose-coloured, the solutions of which present the absorption bands of the salts of didymium, and whose ignited oxides answer to the formula $D_{12}O_3$.
4. *Oxides of lanthanum;* those of the earths whose salts are colourless without absorption rays, which when ignited answer to the type La_2O_3, and whose nitrates deliquesce in contact with moist air.

The following Table sums up the results obtained:—

	Numbers of fractionation (Series I.)	Atomic weights corresponding.
Between 400° and 420°	1	140·3
	2	140·6
	3	140·6
	4	140·6
	5	140·0
Between 430° and 460°	6	135·0
	7	138·0
	8	138·0
Nitrate not decomposed	9	138·0

During these fractionated fusions the didymium first separates, the melted and dissolved mass loses more and more its rose-colour, and after the separation of No. 8 it is colourless; No. 9 then represents lanthanum free from didymium. Thus by a single fractionation we obtain lanthanum exempt from didymium.

The oxalates of the fractions Nos. 1 to 5 yield, on limited ignition in air, an oxide of a brown colour, becoming greyish on ignition to bright redness.

The oxalates of the fractions Nos. 6 to 8 give, on limited ignition in air, a very pale brown oxide, becoming greyish-white at a bright red heat.

The fractions 1, 2, and 3 were collected together, and the whole, in the state of nitrates mixed with five times their weight of saltpetre, was submitted to fractionated fusion between 400° and 420°. There were thus obtained six new fractions (Series II.), and a portion not decomposed, No. 7.

	Numbers (Series II.)	Atomic weights.
Between 400° and 430°	1	135·6—135·1
	2	140·4
	3	142·6
	4	142·9
	5	142·5
	6	141·25
Nitrate not decomposed	7	140·1

Thus the curve of the atomic weights presents two branches, the one ascending, the other descending, with a maximum for No. 4 close upon 143. This anomaly is due to the presence in the first fractions of a certain quantity of earths not belonging to the ceric group. On eliminating these earths by a saturated solution of potassium sulphate, we re-ascend for the precipitated part to a number close upon 143.

Nos. 4 and 5 (Series I.), re-united, were again fractionated by melting the nitrates with 5 parts of saltpetre at 400° and 430°.

	Fractions (Series II.)	Atomic weights.
From 400° to 430°	1	142·15
	2	141·99
	3	141·7
	4	141·48
Nitrate not decomposed	5	138·7

The same has been done with the fractions 6, 7, 8 (Series I.), re-united.

	Fractions (Series II., set 2).	Atomic weights.
From 410° to 430°	1	141·0
	2	141·1
	3	140·5
From 430° to 460°	4	139·4
	5	138·5
	6	138·1
	7	138·0
Nitrate not decomposed	8	138·0

We then re-unite the earths which after the second fusion with saltpetre have given atomic weights between 142 and 143.

	Fractions (Series III.)	Atomic weights.
Between 400° and 420°	1	142·8
	2	143·0
	3	142·8
	4	142·5
Nitrate not decomposed	5	141·6

The earths which after Series III. have given atomic weights above 142·5 are re-united, and divided into two fractions by fusion between 400° and 420°.

Fractions (Series IV.)	Atomic weight.
1	142·8
2	143·1

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* See *Comptes Rendus*, cxx., p. 962, and Chem. News, lxxi., p. 260.

It seems, therefore, that we have reached the limits of the separations, and that the didymium 143 to 143·1 represents that with the highest atomic weight. No. 1 (Series IV.), which gives 142·8, has been further brought by fresh separations to a product showing 143·3.

We have thus fixed approximately the highest atomic weight of didymium between 143 and 143·5.

The treatment of monazite, conducted almost like that of cerite, has yielded, among the earths separated between 410° and 460° by melting the nitrates with saltpetre, an oxide which, after a careful elimination of the bases alien to the cerite group, gives very rose-coloured salts, showing the absorption rays of neodymium, and giving for the atomic weight of the corresponding metal a value close upon 137·5.

I have reason to think, after numerous experiments into the details of which I cannot here enter, that between these two limits, 137·5 and 143·5, there come other earths all showing the properties of didymium, especially an earth the atomic weight of whose metal will be close upon 140. It may still be possible that this last earth may be divided into the two extremes by suitable procedures. For the present we leave this question open.

In the foregoing we have disregarded praseodymium, the salts of which are green, and which on our methods of separation has revealed itself only by the absorption-rays.

Some experiments in course of execution have also shown us that lanthanum oxide (defined as above) may be resolved into at least two earths, one of which would have for the atomic weight of its metal a number near 138, whilst the other would have a value near 135. This latter point will form the object of a closer investigation.

As for the didymiums, the nitrates present a resistance to decomposition in the inverse ratio of the atomic weight. The earth with the lowest atomic weight accumulates in the latter parts of the treatment.

In the whole of these researches I have again utilised as means of separation:—1. The fractionated crystallisation of the sulphates in heat; the sulphate corresponding to the lowest atomic weight accumulates generally, as in the case of cerium, in the mother-liquors. 2. The different solubility, in cold and heat, of the double potassium sulphates, which present the same peculiarity.

These experiments will be continued in the hope of explaining the questions left doubtful, and of doing away with the marks of interrogation put in the bulky record of my numerical determinations.

The question must also be studied from the spectroscopic point of view. In the above we have taken as a criterion the atomic weights aided by the absorption spectra.—*Comptes Rendus*, cxx., p. 1143.

THE DECARBONISATION OF BONE-BLACK.*

By WILLIAM D. HORNE, Ph.D.

The chief value of the enormous quantities of bone-black annually used in refining sugar, glucose, mineral and other oils, &c., lies in its power to withdraw from solutions the contained organic colouring matters. After the liquid under treatment has run for some time over the bone-black, the absorption of colouring matter by the latter is seen to diminish, and when this has proceeded to a certain point the supply is cut off and the bone-black subsequently washed with water, naphtha, or other appropriate solvent to wash out, as far as possible, the colouring matters, &c., which have been absorbed by the bone-black. In spite of the most careful washing, however, some carbonaceous matter persistently clings to the char, to remove which the bone-black is heated in closed iron pipes or retorts in kilns without the access of air. A destructive distillation of the carbonaceous matters results, driving out a large proportion of their substance in gaseous form, but still leaving a small quantity of their carbon deposited in the pores of the grains of bone-black. This accumulation of carbon is quite slow, and the char may be used about a hundred times in refining high grade sugars before its pores become so thoroughly choked as to destroy its usefulness. The deterioration is more rapid for low grade sugars; and in refining petroleum the deterioration is so excessive that a dozen treatments will often exhaust the char. Thus the sugar refiner finds his char exhausted in about a year, and the oil refiner much sooner. Other minor changes take place in the char, of course, but none which can compare in destructiveness to this accumulation of carbon.

When it is remembered that about three tons of bone-black are needed in a sugar refinery to each ton of sugar represented in the daily melt, and that while new bone-black costs upwards of forty dollars a ton, the discarded char brings only about one-third of that price, it will be appreciated what a heavy annual investment the purchase of new bone-black entails. Some unsuccessful attempts to obviate this difficulty had been made by others, but the distinction of overcoming it belongs to Mr. Moriz Weinrich, who is already world-renowned as the inventor of the steam washing centrifugal machine which bears his name.

He has recently invented and patented processes and apparatus for radically improving the quality of old bone-black. One process consists of the complete removal of carbon from the bone-black, and the artificial introduction of fresh carbon in smaller quantity. The other consists of a uniform partial removal of carbon when that element is excessive. The first is applicable to exhausted char, such as sugar refineries and oil refineries discard. The second is preferable for removing small percentages of carbon from bone-black which has begun to deteriorate through the choking of its pores with carbon, but which has not reached the limit of usefulness. In the first case all of the carbon is burned out by passing the bone-black in a small continuous stream through the inventor's apparatus, a nearly horizontal cylinder of sheet-iron, which is heated to a dull red and rotated constantly. The char enters the drum through a central orifice in the head closing one end, which is slightly higher than the other, and leaves the drum through peripheral openings in the head of the lower end. Within the drum longitudinal projecting ribs serve to expose the bone-black more completely to the hot air in the drum. The air enters at the openings in the lower end of the drum and either wholly or partially oxidises the carbon in the bone-black, depending upon the heat of the drum, the volume of air, the amount of bone-black fed into the drum, the speed of turning, &c.

In case the carbon is all removed, the mineral frame-work remains intact with its pores opened up. This bone-black can then be treated with a solution of glue, molasses, or or other carbonaceous matter to thoroughly impregnate it. Then the whole can be rendered thoroughly dry and submitted to destructive distillation in closed retorts without the access of air. The organic matter is hereby charred in the very pores of the grains of bone, and the carbon thus deposited seems to be exactly similar to that originally present. After the above re-carbonisation the grains must be washed with hot water to remove soluble substances, and then the char is ready for use.

In the case of partial decarbonisation, only one operation—that of passing through the drum—is necessary, where a high carbon char can be reduced to a low carbon char, and the process regulated to remove any percentage required. Washed char, fresh from the filters, and containing those organic matters which are usually destroyed by destructive distillation in retorts or kilns, can be thoroughly cleansed by passing it through this apparatus at a heat below redness which indicates the possibility of this method replacing the present method of purification or revivification in kilns.

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* Read before the New York Section of the American Chemical Society, April 12, 1895.

These methods have been investigated and tested by the author in the laboratory and on a working scale in their relations to sugar refining, with eminently satisfactory results, as shown below. Some unfavourable results have at times appeared, but they have been due to removable causes, or have been so slight as to be negligible in consideration of the great advantages attained.

A quantity of old bone-black discarded from a sugar refinery, and containing in the neighbourhood of 20 per cent of carbon, was heated in the open air until it was burnt white. Sufficient low grade sugar syrup for its dry substance to be equal to about 15 per cent of the weight of the decarbonised char was diluted with hot water and then thoroughly mixed with the burned bone, then evaporated to dryness, and put into an iron tube closed at one end and having only a small vent in the cap at the other end, and heated to a dull red until all the gas was given off. This carbonised bone was then cooled and washed with water, to remove all soluble matter, and dried. It now resembled new char in appearance, but contained only about 5 per cent of carbon. 300 c.c. of this char was put into a litre bottle with 350 c.c. of a solution of molasses-sugar, 33° Bé. and exponent or coefficient of purity equal to 89·2, and heated one and a half hours in a water-bath at 175° F. with frequent agitations. New char was washed similarly and dried and subjected to the same treatment. The solutions were then filtered off, and while both had been greatly lightened in colour, that from the re-carbonised char was considerably lighter than that from the new char. The exponent of the former was 93·0; that from the latter 92·4. The char samples were carefully washed and heated in closed tubes, as before, to remove the impurities, and again treated as before. In all these two samples were submitted to nine successive treatments with very dark sugar solutions, the object being to ascertain whether the artificially carbonised char would stand use as well as ordinary char; and it was found that while both samples deteriorated greatly owing to the large amount of work which had been put upon them, the treated char was relatively as much better than the other sample at the end as it had been at the beginning so far as colour was concerned.

The new char had increased the exponent 0·17 per cent more than the treated char in the average of all nine tests; but while the new char had removed 66·6 per cent of the colour from the average solution, the re-carbonised char had removed 83·3 per cent.

A decarbonising apparatus was built consisting of a cylindrical drum of $\frac{3}{16}$th-inch wrought iron 9½ feet long by 2½ feet in diameter, with a central longitudinal shaft by which it is turned. The drum has a slight inclination from the horizontal, and is provided with internal longitudinal ribs to raise the char a little way on the ascending side as the drum revolves. The whole is enclosed in brick-work and heated by a fire built beneath its lower end. By means of this either a total or a partial decarbonisation of char can be effected, and the amount to be burned off can be regulated to a nicety by proper adjustments.

Bone-black that had been in constant use nearly a year, and containing 12 per cent of carbon, was reduced to about 9 per cent of carbon and tested in the laboratory against the untreated char by the above-mentioned filtration process. The original solution used had a colour equal to 200 on an arbitrary scale. The filtrate from the untreated char had a colour of 80, and that from the treated char a colour of 27. In another test the original solution had a colour of 240.

Filtrate from untreated char	110
,, treated ,, ...	20
,, overtreated char (some white grains) ..	26

The same samples of char, after draining, were treated again with a slightly less amount of sugar solution.

Filtrate from untreated char, colour = ...	120
,, treated ,, ,, ...	40
,, overtreated char ,, ...	50

In the two treatments the—

Untreated char removed	52·5	p. c. of the colour present.	
Treated ,,	87·9	,,	,,
Overtreated ,,	84·5	,,	,,

It was thought that these tests, extending over one and a half or two hours, might show a greater difference between the samples than tests extending over a longer period, and so the following experiment was made:—

300 c.c. of each char was heated at 175° F. with 600 c.c. Muscovada sugar solution at 27° Bé., giving the following results. The original solution had a colour of 210.

	1½ hours.	6 hours.
Filtrate from house char, colour =	50	12
,, new ,, ,,	40	10
,, treated ,, ,,	20	7

Showing that the treated char held its own very satisfactorily. Further, a series of six consecutive treatments of new char, char several months in use, and the same after partial decarbonisation, was made. 300 c.c. of each black was heated at 175° F. with 600 c.c. Muscovada sugar solution at 27° Bé. for ten hours, being shaken every fifteen minutes. The char was thoroughly washed, and heated in nearly closed tubes after each absorption test. The average colour of the liquor going on was 152·5, and that coming off was—From the house char, 22·8; from the new char, 16·4; from the treated char 16·7. The treated char, although a trifle below the new char in the final average, actually deteriorated less during the test than either of the others, and thus showed a relative improvement at the end of the experiment.

Many tests have been made on the working scale which have demonstrated the superiority of the decarbonised char over old char, and its equality in many respects to new char. In the first of these tests a filter of house char containing 12·32 per cent of carbon, and another of decarbonised char containing 10·04 per cent of carbon, had equal quantities of the same liquor run over them for a prolonged period, forty-nine and a quarter hours. The average liquor from the house char had a colour of 25, while that from the treated char had an average colour of 15; and it was very striking that the difference in colour increased as the test proceeded, the latter part of the liquor from the untreated char averaging 50, while the corresponding portion from the treated char averaged only 25. The house char withdrew 79·88 per cent of the colour present, while the treated char withdrew 87·69 per cent. In another set of filtrations on the working scale in a sugar refinery a raw sugar solution, colour 120, Bé. 27·7°, and exponent 90·09, was put in the regular course of running through filters of char respectively several months old, new and decarbonised. The average colour of that from the old char was 23, from new char 19, from the partially decarbonised char 18. The exponents scarcely varied, being respectively 92·17, 92·37, 92·09.

These are a few of a great many tests, both in the laboratory and in the factory, made upon char which had been partially decarbonised in a small working model which could not be controlled with the desired nicety, while the average percentage of carbon in the decarbonised char was 10·04 per cent, or 2·28 per cent less than in that from which it was prepared, there was a good deal of it which through different causes still contained more than 11 per cent of carbon, and considerable which had been so overburned as to be rendered weak as a decolouriser. These two extremes, while giving a favourable-looking average percentage of carbon, both deteriorated the char for the purposes in hand. Some improvement having been made in the operation of the decarbonising drum, which, however, is still far inferior to what the inventor's design calls for, it has been possible to turn out a much more uniform product. The carbon can be reduced to any desired point and kept to within ½ per cent of the requisite figure. Having thus prepared another large quantity of char, sufficient for factory tests, another experiment was made. The carbon this time was reduced from 13·03 per cent to 10·22 per cent, and two filters filled with these grades were run against each other. The liquor entering had a colour of 110. The average of that coming from the untreated char was 10, while that coming from the treated char, all the conditions being carefully kept precisely similar, was only 5. From the old char the liquor ran water-white for less than one hour; from the decarbonised char it ran water-white for more than five hours, and at the end of the run the liquor from this filter was only about as dark as that at the middle of the run from the filter of ordinary char.

Now, as to the changes in the bone-black itself after a partial decarbonisation. Microscopic examination shows the decarbonisation to be uniform throughout the grain. Two analyses made to illustrate the chemical changes may be quoted:—

	Before decarb. Per cent.	After decarb. Per cent.
Carbon	12·32	8·90
Calcium carbonate ..	3·32	3·26
Iron	0·32	0·21
Calcium sulphate . ..	0·904	0·877
,, sulphide . ..	0·628	0·494

The most noticeable, and in fact the most desirable, changes are the reduction of carbon with a corresponding opening of the pores and increase in absorbing power, and the reduction of calcium sulphide, which is very important for sugar refineries, in view of the deleterious action this substance exercises upon the sugar. Numerous experiments showed that the carbonate of lime is not decomposed by the mild heat which suffices for oxidising the carbon, and the slight decrease indicated above is doubtless due to variations in samples or error of analysis. The friction of the grains of bone-black against each other in the drum is so slight that very little dust is formed. Samples taken to represent as nearly as possible the same char before and after treatment showed percentages of dust as follows:—

	Before treatment. Per cent.	After treatment. Per cent.
Finer than 30 mesh ..	12·56	12·64
,, 50 ,, ..	0·96	2·20

The bone-black becomes specifically lighter in proportion to the carbon lost, but this does not show in the determinations of sp. gr. probably because of the grains packing more closely after treatment. This indicates a wearing off of some sharp corners of the grains. A quantity of bone black, which before treatment had a sp. gr. of 1·0624 and lost 2·81 per cent of carbon during treatment, had a sp. gr. of 1·0636 afterward.

As might be expected, the process of opening the choked pores renders the bone-black slightly more friable, as shown by the fact that a sample which before treatment gave 1·76 per cent of dust by the method described by the author in a previous paper (Chemical News, lxxi., p. 42), gave 2·84 per cent after treatment. This, however, is scarcely more than is given by some new bone-blacks.

The great advantages of these inventions, then, are quite apparent. The refiner of oil, sugar, or glucose who uses large quantities of bone-black need not discard it at a great loss after its pores are choked with carbon and its decolourising power lost; but he can, by a very simple and inexpensive process, bring it back to its original decolourising power, when it will last nearly, if not quite, as long as before. But by far the greater advantage is the possibility of preventing its ever getting into bad condition by submitting it to the decarbonising process while yet the carbon is only slightly above the normal for new char, and thus keeping it always at its maximum efficiency.

By a careful use of this apparatus it is possible to burn off the organic impurities persisting in bone-black after washing instead of charring them as in the ordinary method of revivifying in kilns with the exclusion of air; and it is not at all impossible that the apparatus will in the near future supersede the present kilns used in all factories employing large quantities of bone-black.

Yonkers, N.Y.

ON INDISCRIMINATE "TAKING."

By PETER T. AUSTEN.

In many of the text-books which have of late appeared, and even in articles by some of the most renowned chemists, the verb "to take" is frequently used in a way that is very annoying to teachers who are endeavouring to train students in brevity and exactness of expression. Pages could be filled with examples of bad style and verbosity that ill accord with the clearness and brevity that are desirable, and that are supposed to characterise scientific literature. A few quotations from recent text-books will suffice ao illustrate this particular case—that of indiscriminate "taking."

"Take a cylindrical porous jar, such as is used in a galvanic battery, close the open end," &c.

It were better to say—"Close the end of a cylindrical porous jar, such as is used," &c.

Another example—"Take two flasks and connect them."

Better—"Connect two flasks," &c.

Another—"The method of experimenting adopted by Graham was to take a bottle or jar with a neck contracted somewhat and fill it to within half an inch of the top with the solution of the salt to be investigated."

Better—"The method . . . was to fill a bottle or jar with a somewhat contracted neck to within half an inch," &c.

Another—"If we take an iron tube closed at one end and connected at the other with a Sprengel pump and exhaust it completely."

This awkward form of diction often excites mirth in the class room, as it gives unusual opportunities for double meanings.

"Take a pound of sugar and an equal weight of sulphuric acid." This would be a severe dose even for a trained scientist.

The following is from a recent text-book—"Take a lump of chalk or sandstone, some very dry sand, a glass of water, and a glass of treacle."

This might do for a bill of fare in a Chinese restaurant, but it is out of place in a scientific book.

"Take some white arsenic,"—"Take a seidlitz powder,"—are the singular directions which preface two experiments in a book recently published by the Society for Promotion of Christian Knowledge, London.

If editors and teachers will pay more attention to this awkward use of the word "take" they will incur the gratitude of a patiently suffering public.—*Science.*

Polytechnic Institute of Brooklyn.

"**Who Discovered the Circulation of the Blood?**"—An amusing story was recently told by a lecturer who perambulates the country giving popular lectures on Physiology in rural parts. The chairman upon one occasion was a clergyman, who, knowing nothing of the subject of the lecture—namely, "The Circulation of the Blood"—hurriedly consulted a cyclopædia before taking the chair. He introduced the lecturer as follows:—"Ladies and gentlemen,—You are going to-night to listen to a lecture on the heart and the circulation of the blood. Perhaps you would like to know who invented the circulation. The circulation was invented by a person of the name of Harvey, and if you are anxious to know who Harvey was I can tell you that he wrote the 'Meditations amongst the Tombs' and discovered Harvey's sauce for fish."—*Medical Press and Circular.*

CORRESPONDENCE.

THE USE OF THE TWADDELL SCALE FOR SOLUTIONS LIGHTER THAN WATER.

To the Editor of the Chemical News.

Sir,—In a review appearing in the Chemical News (vol. lxxi., p. 268) on Redwood's "Theoretical and Practical Ammonia Refrigeration," appear the words:—"Of course Twaddell, being only adapted for solutions specifically heavier than water, cannot be used for ammonia." There appears to me no reason why Twaddell should not be adapted for solutions lighter than water, as follows:—

$$\begin{aligned} 1{\cdot}005 \text{ sp. gr.} &= +1^{\circ} \text{ Tw.} \\ 1{\cdot}000 \quad \text{,,} &= \;\; 0^{\circ} \;\; \text{,,} \\ 0{\cdot}995 \quad \text{,,} &= -1^{\circ} \;\; \text{,, \&c.} \end{aligned}$$

There is no reason, as far as I can see, why we should not have minus degrees Twaddell for solutions lighter than water in the same way that we have minus degrees Centigrade for temperatures below the freezing-point of water. The Twaddell hydrometer for the minus degrees could be marked in red letters on the stem to distinguish them from the plus degrees. The reading for minus degrees would be read from the bottom of the stem upwards. The rule for the conversion of degrees Twaddell into specific gravity would become—

$$1000 \pm x^{\circ}. \times 5.$$

By this means "our old enemy Baumé" might be easily dispensed with.—I am, &c.,

Clayton Beadle.

VOLUMETRIC DETERMINATION OF SUGAR BY AMMONIO-CUPRIC SOLUTION.

To the Editor of the Chemical News.

Sir,—In the Chemical News for May 24 (vol. lxxi., p. 257) my assistant and demonstrator, Mr. Peska, and myself, who communicated Mr. Peska's paper to the Chemical Society, are charged with unjust action by Mr. Allen, who says that we have "appropriated" and "annexed" his scientific idea, namely, the discovery that a layer of mineral oil protects an ammoniacal cupric solution from oxidation by air. In agreement with Mr. Peska, I beg to answer as follows:—

The above method was practically used by Mr. Peska in October, 1893, as I can prove, if necessary, by trustworthy scientific witnesses. The original paper of Mr. Allen was *not known* to me or to Mr. Peska, for *The Analyst* is inaccessible to us, and I am sorry to say that my time and scientific occupation do not allow me to read other than first-class English chemical journals, the rest being known from abstracts only. So I know Mr. Allen's paper on the "Examination of Urine for Small Quantities of Sugar" only from an abstract in the *Chem. Soc. Journ.*, Dec., 1894, p. 488. The abstractor does not refer to the use of mineral oil, being probably not struck by the great scientific importance of that discovery.

I confess I had no wish to read a paper in full, the end of which contains the "novelty" that the best test for traces of sugar in urine is the well-known phenylhydrazine.

Mr. Peska, in his original paper, and in my abstract of it, speaks of Fehling's method or its rather lengthy modification by *Soxhlet*." The change of the last name for *Allen* I regard as a misprint which might be explained by one of the Secretaries of the Chemical Society, *who alone* are responsible for the abstracts in the *Proceedings*. I got no letter from the Secretary on that point whatever.

Mr. Peska's intention was certainly not to quote all papers on the determination of sugars, and especially not of sugar in urine, as that of Mr. Allen, for it alone would have filled several pages and would be of no use. If the manipulative device found by Peska in 1893 was not published *at once*, it is owing to a principle of our laboratory to publish scientific work after some results worth publishing are obtained, even if it may take ten years or so. The otherwise practical device of using vaseline oil I do not consider to be the principal merit of Mr. Peska's paper; I see it in the fact that he has minutely worked out a method, not only of determining *sugar in urine*, but of accurately determining glucose, invert sugar, same in presence of saccharose, then maltose, lactose in solutions of all concentrations, and of studying the interesting behaviour of dextrines, as will be seen soon from the full paper.

I should have never entered into the discussion of the mere priority of the use of vaseline oil had I not been attacked by Mr. Allen. Instead of charging us with dishonest action, Mr. Allen had better sent me a copy of his paper and I should have given him private information. I should have given him all possible satisfaction if I had found that his method is so beautifully worked out that it makes Mr. Peska's paper superfluous. I conclude, however, from the said abstract that there is a great difference in this point between the paper of Mr. Allen and that of Mr. Peska.—I am, &c.,

Bohuslav Brauner.

Bohemian University, Prague,
June 2, 1895.

"STEEL WORKS ANALYSIS."

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lxxi., p. 268) there appears a letter from my friend Mr. William Galbraith in which he suggests that I was unintentionally unfair in my criticism ("Steel Works Analysis," p. 152) of his admirable process for the volumetric determination of chromium in steel. He seems to object to the expression "modified method," although in the same paragraph it was stated that as far as possible the simplicity of the original process had been preserved. As Mr. Galbraith surmises, I had no intention of being unfair, and after carefully considering the matter have come to the conclusion that Mr. Galbraith has no ground whatever for complaint. As he says, I am "anxious that the process should live," and, consequently, I have made a very large number of experiments on the method and devoted six pages of my book to its consideration. Practically, the whole matter lies in a nutshell. Mr. Galbraith, in his original method, advised the use of about 1¼ grms. excess of permanganate, or about six times too much. He oxidised in 60 to 70 c.c. of liquid containing 18 grms. of strong sulphuric acid. Under these conditions, in steels containing 2 or three per cent of chromium, the results are always seriously low: First, because the large manganic precipitate always carries down some chromium with it; second, in a solution so strongly acid, the complete oxidation of Cr_2O_3 to CrO_3 is practically impossible.

Some two or three years ago I modified the process (and at the meeting of the Sheffield Metallurgical Society fully described the modification in Mr. Galbraith's presence) by employing only 0·2 grm. excess of permanganate, and oxidised in a total volume of about 150 c.c.; under these conditions the results are accurate. In fact the alterations which Mr. Galbraith objects to as being so "trivial" and "unfair" as not to constitute any "modification" (I know of no other word to use), determine the difference between reliable and worthless results.

With reference to Mr. Galbraith's new soda process, it is certainly the general impression that he designed it to replace the old method, and that it was applicable to chrome steels.

Mr. Galbraith mentions the fact that Mr. Stead has described a modification of the permanganate process. If Mr. Galbraith will take the trouble to refer to p. 157

et seq. of "Steel Works Analysis" he will find this process favourably criticised and fully described.

Mr. Galbraith is evidently hyper-sensitive to criticism, even of the mildest description, and his own florid denunciation of my gravimetric process seems to have escaped his memory. He declared at the meeting of the Sheffield Metallurgical Society, to which he refers, that the method gave results "50 per cent too high"—a rash assertion, which the personal experience of several steel work's chemists present, to say nothing of my own exhaustive experiments, proved to be absolutely inaccurate.

Steel chemists are much indebted to Mr. Galbraith for devising the broad principle of a rapid and beautiful volumetric method for the estimation of chromium in steel. Unfortunately, however, the process is essentially empirical, and its success depends on a rigid adherence to special details; the latter were not accurately described by Mr. Galbraith, and, in consequence, many chemists abandoned the method as unreliable. Now, because I have endeavoured to restore confidence in the process by pointing out where it may go wrong, and how to avoid error, Mr. Galbraith, so far from being grateful, considers I am "unfair." I am content to leave the matter to the judgment of steel work's chemists.—I am, &c.,

J. O. Arnold.

The Technical School, Sheffield,
June 10, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 21, May 27, 1895.

Nomination of a Foreign Associate.—The Academy proceeded to nominate a foreign Associate *vice* the late Professor Van Beneden. The number of voters was 48. Dr. E. Frankland received 43 votes; Prof. Sir G. G. Stokes, 3 (!); Mr. Newcomb, 1; Herr Suess, 1. Dr. Frankland having obtained an absolute majority of the votes was proclaimed elected.

The Academy then proceeded to nominate a commission to draw up a list of candidates for the position of Foreign Associate *vice* the late Herrn von Helmholtz. The commission includes three members on behalf of the sections for mathematical sciences, MM. Bertrand, Fizeau, and Tisserand, and three on behalf of the sections for physical sciences, MM. Berthelot, Daubiée, and Van Tieghem.

Contribution to the History of the Earths of Cerite.—P. Schützenberger.—(See p. 288).

Accumulation in the Soil of Cupric Compounds used to Combat the Parasitic Diseases of Plants.—Aimé Girard.—The author concludes from a numerous series of experiments that the prolonged use of the compounds of copper for the treatment of the vine or the potato has no effect either upon the quantity or the quality of the produce.

Reduction of Nitric Oxide by Moist Iron or Zinc.—P. Sabatier and J. B. Senderens.—The simultaneous formation of free nitrogen and of nitrous oxide is not established. The nitrous acid falls gradually from 68 per cent during the first hour to 0·0 after a month. The free nitrogen rises from 32 during the first hour to 75·3 from the fourth to the fifth day, and then falls; after one month to 63·1; and after two months to 48. The hydrogen increases from 1·7 from the second to the seventeenth hour to 52 after two months.

The Reduction of Silica by Aluminium.—M. Vigoreux.—It appears that there are two modifications of silicon, the one amorphous and the other crystalline and in thin layers transparent.

Certain Reactions of Lead Sulphide.—A. Lodin.—Lead sulphide enters into fusion only at 935°, but its vapour tension is considerable at much lower temperatures. This latter property explains the phenomena of volatilisation ascribed by Hannay to the hypothetical compound PbS_2O_2, as also to the active development of the reactions of PbS upon PbO and $PbSO_4$ at temperatures below 935°. At these temperatures the formulæ admitted long ago to explain the reactions of the metallurgy of lead are exactly verified.

On the Campholenic Derivatives.—A. Béhal.—The author considers the active and inactive campholenic acids as stereoisomers.

On Crystalline Cinchonicine.—Ferdinand Roques.—This substance has hitherto been known only as vitreous and resinoid, but the author has obtained it in anhydrous amber-yellow crystals, forming crystals of often more than 10 m.m. in length by 3 m.m. in breadth, but presenting curved surfaces. Their optical properties indicate a triclinar form. They are soluble in benzene, toluene, acetone, chloroform, and alcohol (absolute or aqueous), but they have not hitherto been re-crystallised from these solutions. The author is continuing his researches, and extending them to quinicine.

Transformation of a Salt of Aniline into Acid Aniline.—L. Simon.—The author maintains anilephenylglyoxylic acid is entirely transformed by boiling water into aniline phenylglyoxylate.

On Ozobenzene.—Adolph Renard.—Ozobenzene is an addition product in which the six supplementary atomicities of the benzenic nucleus are saturated by six atoms of oxygen connected to each other two by two, one atomicity.

The Fixation of Iodine by Potato-starch.—Gaston Rouvier.—Whilst the starches of wheat and of rice, produced by one and the same vegetable family, behave in the same manner with iodine, that of the potato, produced by a very remote family, behaves in a totally different manner.

Elimination of Magnesium in Rachitic Patients.—Oechsner de Coninck.—The author notices the minute proportion of magnesium eliminated in the urine of the rachitic cases examined.

Journal fur Praktische Chemie.
New Series, Vol. li., Parts. 1 and 2, 1895.

Contributions to a Knowledge of the Arsenites.—A. Stavenhagen.—The author describes here the potassium ortho-, meta-, and pyro-arsenites, besides the two salts $K_2As_4O_7+2H_2O$ and $K_4As_6O_{11}+3H_2O$; the sodium ortho-, meta-, and pyro-arsenites; the ammonium ortho-, meta-, and pyro-arsenites; the corresponding calcium, strontium, and barium salts; the magnesium ortho- and pyro-arsenites; the zinc and cadmium ortho-arsenites; the mercurous and mercuric ortho-arsenites; the copper ortho- and meta-arsenites; the silver ortho- and pyro-arsenites, with Girard's salt, $Ag_6As_4O_3$; the auriortho-arsenite; the thallium ortho-arsenite; the stannous and stannic ortho-arsenites; the lead ortho-, meta-, and pyro-arsenites; the bismuth arsenite; the chromium arsenite; the manganese ortho- and pyro-arsenites; the iron arsenite. It is here remarked that the favourable action of ferric hydroxide in cases of arsenical poisoning is due to the fact that it prevents the formation of hydrogen arsenide. The author further describes cobalt ortho- and pyro-arsenite, and the compound $Co_3As_4O_9+4H_2O$; nickel arsenide; platinum ortho-arsenite, and platinum oxide-ammonium arsenite.

Synthetic Experiments in the Pyrazol Series. Part I.—R. von Rothenburg.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These researches include a discussion on the isomeric diazobenzene potassium sulphite, by Ad. Claus; and a memoir by Alb. Edinger, on the aromatic amines, sulphidised in the nitrogen.

On Pyro-antimonic Hydroxide.—C. Serono.—The author infers from his researches that the hydrate $Sb_2O_32H_2O$ does not exist.

On Two New Laboratory Appliances.—C. V. Schön.—This paper cannot be abstracted without the insertion of the two accompanying figures.

The Combination-Heat of the Crystalline Water of Organic Compounds.—W. J. Jorissen and E. van de Stadt.—A series of thermo-chemical determinations.

Some Experiments on Oxidation by Partial Combustion.—J. Walter.—Hitherto there was known only a single instance of the production of one substance from another by a partial combustion, *i.e.*, that of formaldehyd from methylic alcohol. The author has been engaged with experiments in this direction, but he has never obtained results even approaching those of formaldehyd.

Remarks on the Work of Curtius and Dedichen: "Synthesis of Benzenehydrazines by means of Hydrazine Hydrate."—A. Purgotti.—Already inserted.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 5, 1895.

A Regulator of Temperature.—M. Berlemont.—This apparatus cannot be described intelligibly without the accompanying figure.

On Certain Addition-Derivatives of Ferric Chloride and Nitric Oxide.—V. Thomas.—Nitric oxide reacts very slowly in the cold upon ferric chloride, forming a definite brown powder. If the temperature is raised to 40° we obtain a red substance. The compound obtained in the cold consists of $Fe_2Cl_6.NO$. The substance formed at from 40° to 60° consists of $2Fe_2Cl_6.NO$. Both these substances are very hygroscopic. They are decomposed in contact with water, losing the nitric oxide which they have absorbed. They are fusible in sealed tubes without decomposition. If heated in the open air they are transformed into ferric oxide. The author has not been able to obtain them in crystals.

Cyanic Ethers and Nitriles of the Alcohols.—Albert Colson.—The author has exposed to the sun a mixture of washed ether and cyanogen chloride. The product was methane. On exposing the same mixture to the sun during the whole of summer he obtained an isomer, very stable. The author has further obtained cyanal acetate, propionate, and propylcyanal acetate.

MISCELLANEOUS.

The German Society of Applied Chemistry (Deutsche Gesellschaft für Angewandte Chemie) held its Annual Meeting in Frankfort-am-Main on the 9th to the 12th inst.

The Deutsche Electro-Chemische Gesellschaft held its Annual Meeting in Frankfort-am-Main on the 6th, 7th, and 8th inst. Among the papers read at the meeting were the following:—"Charging Accumulators by means of an Alternating Current," by Herr Pollak; "Calcium Carbide," with experiments, by Dr. Borchers; "On a New Method of Analysis by Electrolysis," by Dr. Jordis; and "Electrical Transmission of Power," by Prof. Ostwald. Visits of inspection were also paid to the Accumulator Works of the Pollak Co., and to the Gold and Silver Separating Works in Frankfort.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 10th inst., Sir James Crichton-Browne presiding. The following were elected Members:—Mr. Benjamin Bennett, Mrs. Henry Burton Buckley, and Mr. William Watson Cheyne, F.R.S. The special thanks of the Members were returned to the Right Hon. Lord Playfair for his donation to the Fund for the Promotion of Experimental Research at Low Temperatures.

MEETINGS FOR THE WEEK.

Wednesday, 19th.—Geological, 8.
— Microscopical, 8.
— Meteorological, 7.30.
— Institution of Mining and Metallurgy, 8.
Thursday, 20th.—Chemical, 8. Extraordinary General Meeting to consider change in Bye-law I. The business of the Ordinary Meeting will follow. Ballot for the Election of Fellows. "On Lintner's Isomaltose," by Horace T. Brown, F.R.S., and G. H. Morris, Ph.D. "Transformation of Ammonium Cyanate into Urea," by Prof. Walker, D.Sc., and T. F. Hamley. "Some Derivatives of Humulene," by A. C. Chapman. "Note on Thio-Derivatives of Sulphanilic Acid," by Miss Walter. "The Chlorination of Orthochlorotoluene" and "The Six Dichlorotoluenes," by W. P. Wynne, D.Sc., and A. Greaves. "The Disulphonic Acids of Toluene and of Ortho- and Para-chlorotoluene," by W. P. Wynne, D.Sc., and T. Bruce. "Ethereal Salts of Ethane-tetracarboxylic Acid," by Prof. Walker, D.Sc., and J. R. Appleyard. "Method for Preparing Formyl Derivatives of Aromatic Amines" and "A Modification of Zincke's Reaction," by H. R. Hirst and J. B. Cohen, Ph.D. "New Method of Preparing Cyanuric Acid," by W. H. Archdeacon, B.Sc., and J. B. Cohen, Ph.D.
Friday, 21st.—Quekett Club, 8.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1856.

ON THE

NEW GAS OBTAINED FROM URANINITE.*

(Fourth Note).

By J. NORMAN LOCKYER, C.B., F.R.S.

Continued experiments on the gases obtained by heating the minerals bröggerite and euxenite *in vacuo* have revealed the presence in the spectrum of an important line in the infra-red. By comparisons with the solar spectrum in the first order grating spectrum, the wave-length of the line has been approximately determined as 7065. There can be little doubt, from the observations which have been made, that this new line is coincident with the chromospheric line which occurs in Young's list, having a frequency of 100, of which the wave-length on Rowland's scale is stated to be 7065·5.

It follows therefore that, besides the hydrogen lines, all three chromospheric lines in Young's list which have a frequency of 100 have now been recorded in the spectra of the new gas or gases obtained from minerals by the distillation method.

These are as follows:—

7065·5
5875·98
4471·8

The wave-lengths of the lines are in Rowland's scale, as given in Scheiner's "Astronomical Spectroscopy" (Frost's translation, p. 184). In a partial revision of his chromospheric list, Professor Young gives the *corona* line 5316·79 as also having a frequency of 100 in the chromosphere, but, up to the present, this line has not been observed in the laboratory.

CARIUS-VOLHARD ESTIMATION OF HALOGENS.

By JAMES WALKER, Ph.D., D.Sc., and JAMES HENDERSON, B.Sc.

We lately recommended the estimation of halogens in organic compounds by the Carius method combined with the Volhard method of silver titration (Chemical News, lxxi., p. 103). Shortly after the appearance of our communication, Dr. F. W. Küster published a paper in *Liebig's Annalen* (cclxxxv., p. 340) on the same subject, in which he rejects the method as untrustworthy. The principal source of error under the conditions employed by him is the action of the excess of silver nitrate on the glass of the tubes, whereby a portion of the silver is withdrawn from the titration, and the volumetric results appear too high. Dr. Küster's interesting observations on the extent of this action are undoubtedly correct, but, as he himself shows, the disappearance of the silver from the solution is largely dependent on the temperature to which the tubes have been heated, the action being very slight at temperatures below 280° and increasing rapidly above 300°. His method of halogen estimation is to heat the sealed tube for two hours at 320° to 340°. In our opinion this temperature is only necessary in very exceptional cases, if a somewhat greater amount of nitric acid is used than Dr. Küster recommends.

Halogen compounds of the fatty series are in general easily decomposed, and it is with aromatic compounds that any difficulty is experienced. We find, however, that if for 0·1 grm. of substance 2 c.c. of nitric acid, of sp. gr. 1·5, are taken, the decomposition is complete after heating for three hours at 250° to 260°, and the action on the glass is so slight as to cause no perceptible difference between the gravimetric and volumetric estimations. The glass we employ is Schott and Co-'s Jena combustion tubing, which can be easily worked at the blowpipe and is of excellent quality, the same tube bearing repeated heating with the acid. The inner tube, to contain the substance, we make of ordinary hard glass tubing.

Dr. Küster only employs 16 to 20 drops of the 1·5 sp. gr. acid (¾ to 1 c.c.) to 0·1—0·2 grm. substance, and it probably this circumstance which necessitates the high temperature he employs. As the oxidation progresses water is formed, which dilutes the acid and enfeebles its action. If, therefore, a larger proportion of acid is present from the first, the extent of this dilution is diminished, and the action can be completed at a lower temperature. With 2 c.c. of acid and Schott's glass we have never had a tube burst.

As para-dichlorobenzene was one of the substances with which Dr. Küster experimented, we made one or two determinations of the halogen it contained, both gravimetrically and volumetrically, with the same portion. In no case could the smell of undecomposed chloride be detected on boiling the diluted solution after heating.

I.

0·1459 grm. of para-dichlorobenzene was heated with 0·4049 grm. $AgNO_3$, and 2 c.c. nitric acid, sp. gr. 1·5, for 3½ hours, at 257°. 0·2907 grm. AgCl was obtained, and the filtrate required 7·25 c.c. of sulphocyanate solution (1 c.c. = 0·00812 $AgNO_3$) for complete precipitation.

Chlorine found, gravimetrically.. .. 49·3 p.c.
„ volumetrically .. .. 49·5 „

The percentage of chlorine in $C_6H_4Cl_2$ is 48·3. The specimen was therefore impure, containing too much chlorine. It was re-crystallised from ether, and another analysis performed.

II.

0·1422 of para-dichlorobenzene was heated as before with 0·4201 grm. $AgNO_3$, and 2 c.c. nitric acid. 0·2796 grm. AgCl was obtained, and the filtrate from this required 10·95 c.c. sulphocyanide solution (1 c.c. = 0·00812 grm. $AgNO_3$).

Chlorine found, gravimetrically.. .. 48·6 p.c.
„ volumetrically .. .. 48·6 „

The re-crystallisation had apparently effected a considerable purification of the substance.

The following numbers were obtained for para-dibromobenzene, the preparation being from Kahlbaum in Berlin:—

III.

0·1186 grm. para-dibromobenzene was heated as before with 0·2061 grm. $AgnO_3$, and 2 c.c. nitric acid. 0·1903 grm. AgBr was obtained, and the filtrate required 3·35 c.c. sulphocyanide solution (1 c.c. = 0·00982 $AgNO_3$).

Bromine found, gravimetrically.. .. 68·3 p.c.
„ volumetrically .. .. 68·7 „

The filtrate from the silver bromide was here decidedly turbid. The calculated amount of bromine in $C_6H_4Br_2$ is 67·8 per cent. As in the case of the chloro-compound the preparation contains too much halogen.

We found that the turbidity of the filtrate might be prevented by adding a little concentrated sulphuric acid to the contents of the sealed tube, and the following estimation, with the same compound as before, will serve as an example:—

IV.

0·1203 grm. para-dibromobenzene was heated with 0·2019 grm. $AgNO_3$, 1·5 c.c. nitric acid, and 0·5 c.c.

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* A Paper read before the Royal Society, June 13, 1895.

concentrated sulphuric acid, for 3 hours, at 250°. 0·1943 grm. AgBr was obtained, and the perfectly clear filtrate required 2·65 c.c. sulphocyanide solution (1 c.c. = 0.00983 grm. $AgNO_3$).

Bromine found, gravimetrically.. .. 68·7 p.c.
" volumetrically.. .. 68·8 "

The agreement of the numbers obtained by the two methods shows that the action of the silver nitrate on the glass, under the conditions given, is negligible. We venture to think that, if these conditions are adhered to, the Carius-Volhard method may be applied with success to practically all fatty compounds, and to nine out of ten aromatic compounds, if not to ninety-nine out of a hundred.

University College, Dundee.

NOTE ON THE PRODUCTION OF CITRIC ACID FROM CANE-SUGAR.

By Dr. T. L. PHIPSON,
Formerly of the University of Brussels, Member of the Chemical Societies of London, Paris, Antwerp, &c.

I have recently made an experiment at the Casa Mia Laboratory, Putney, which is perhaps worth recording. I have found that an acid, which can be no other than citric acid, is produced in notable quantity by the action of permanganic acid on a solution of sugar in the cold.

Some few grms. of cane-sugar are dissolved in water to which a few drops of sulphuric acid have been added, and a rather strong solution of potassium permanganate is poured in. In a short time, at summer temperature, the solution is white and transparent like water. It is neutralised by addition of a little ammonia, and solution of calcium chloride added. No precipitate occurs, which shows the absence of tartaric and oxalic acids, but on boiling the liquid a precipitate occurs which is soluble in acetic acid, and these reactions are characteristic of citric acid. The precipitate being collected and decomposed with sulphuric acid gave a solution which, on being evaporated, gave small but well-formed crystals, which corresponded in form and properties with those of pure citric acid.

If large quantities of permanganate are used, then a notable amount of oxalic acid is produced at the same time.

The Casa Mia Laboratory, Putney,
London, June 17, 1895.

A NEW METHOD OF STANDARDISING ACID SOLUTIONS.

By E. P. PERMAN, D.Sc., and W. JOHN.

On adding dilute sulphuric acid to a solution of borax, sodium sulphate is formed, and boracic acid set free. One molecule of borax requires one molecule of sulphuric acid to neutralise it, using methyl-orange as indicator. This affords a convenient and accurate method of standardising acid solutions. The following are the advantages of the method:—

a, The quantity of borax required is very large; 5 grms. may be taken for a normal solution, and in that case it is unnecessary for ordinary purposes to weigh to less than a centigrm.

b. Borax is readily obtained pure and keeps well. It effloresces slightly in dry air, and should, therefore, be kept in a well-stoppered bottle; in moist air it remains practically unaltered (see Ramsay and Aston on "The Atomic Weight of Boron," *Trans. Chem. Soc.*, 1893, p. 207).

c. The end of the reaction is shown very sharply.

The borax used was in large crystals, and was bought under the name of "refined borax." The following results were obtained with two solutions of different strengths:—

Borax taken. Grms.	H_2SO_4 solution required. C.c.	H_2SO_4 in 1 litre. Grms.	Standardised by Na_2CO_3 solution. Grms.
20·00	53·85	95·28	95·15
12·54	33·90	94·90	
1·985	25·45	19·00	19·02
2·013	27·21	18·98	
2·015	27·26	18·96	

Hydrochloric acid solution may be standardised in a similar way. The results obtained with this acid are given in the following table:—

Borax taken. Grms.	HCl solution required. C.c.	HCl in 1 litre. Grms.	Standardised directly by Na_2CO_3. Grms.
6·588	22·44	56·10	56·07
7·041	23·99	56·08	56·06
			By Na_2CO_3 solution
3·571	36·82	18·53	18·48
3·571	36·89	18·50	

Boracic acid acts upon litmus or phenolphthalein, so that these indicators cannot be used.

The authors think that the method would prove a very useful one for general laboratory use.

University College, Cardiff,
June 15, 1895.

SULPHUR IN OILS.

By WILLIAM FOX and D. G. RIDDICK.

The following Table gives the mean amounts of sulphur in grains per gallon (by weight) that we have obtained from various oils by burning them by means of a floating wick, such as is used for night-lights, and condensing the vapours given off in a sulphur apparatus in the same way as sulphur is determined in coal-gas. Those oils which do not burn alone were mixed with a sufficient quantity of sperm or cocoa nut oil to make them do so without smoking.

Name of Oil.	Sulphur.
Pure Brown Rape	14·2
Ordinary Brown Rape	17·4
Refined Brown Rape, with sulphuric acid	16·8
" " " with Fuller's earth	10·0
Ravison Rape	19·1
*Jamba Rape	113·0
Linseed, La Plata	trace
Sperm, pure	2·3
" Bottlenose	3·1
Cotton-seed	trace
Cocoa-nut, ordinary	3·7
Ground-nut	none
Neat's-foot	4·7
Olive	none
Cod	5·8
Russian Mineral, 0·908	20·5
Russian Burning Mineral	10·3
American Burning Mineral	16·3
American Burning Water White Mineral	8·1
American Burning Safety Mineral	14·0
Scotch Mineral for Gas making	49·8

Liquid Carbonic Acid Works.—Works are being established in Königsberg by a Company known as the Fabrik für Flussige Kohlensäure Oster and Co., for the production of liquid carbonic acid. The plant will have a capacity of 800 to 1000 kilog. per day.

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* Benedikt and Lewkowitsch ("Oils, Fats, Waxes"), state that Jamba oil is free from sulphur.

A METHOD OF DETERMINING THE CRYSTALLISATION OF PRECIPITATES. ZINC AND MANGANESE SULPHIDES, COPPER HYDROXIDE.

By A. VILLIERS

We have already shown that the rate and the temperature of the transformation of amorphous zinc sulphide depend not alone on the composition of the medium in which the precipitation has been effected, but also on changes undergone by this medium after precipitation. Whilst a reduction of temperature retards this transformation, every cause which may produce an effect comparable to a decrease of the dilution of the liquids exerts an inverse action and determines a reduction of the temperature of transformation.

We have thought that the complete congelation of the solvent, being comparable to a concentration carried as far as possible, might enable us to obtain amorphous precipitates in a crystalline state, or at least in an increased state of condensation, notwithstanding the inverse action of a fall of temperature, of slight variations of the ambient medium, involving a variation of the temperature of transformation of more than 100°.

This method seems to be of a somewhat general application, and enables us to obtain easily, by the action of cold, transformations which may be also effected by a rise of temperature, sometimes very considerable. Perhaps these transformations may be ascribed to a different cause, to the compression exerted by the expansion of the ice which imprisons the precipitates. We observe, in fact, after the complete congelation of the liquid produced from the outside to the inside, that the precipitate has been collected in the central part of the block of ice, where it must certainly have undergone a considerable pressure. We have undertaken to ascertain what is the true cause of the transformations thus observed, restricting ourselves at present to giving the three first instances.

Zinc Sulphide.—If we completely freeze the alkaline liquid, holding in suspension amorphous zinc sulphide precipitated from such liquid, and prolong the action of the cold for some hours, we find that, if the liquid is dilute and slightly alkaline after melting the ice, the zinc sulphide is no longer amorphous, and does not re-dissolve, as before the congelation on treatment with a prolonged current of hydrogen sulphide, provided that the volume of the liquid is not too great in proportion to the precipitate.

We may thus, by congelation, transform a precipitate of zinc sulphide, even in media such that the temperature of transformation exceeds 100°.

Manganese Sulphide.—An analogous observation has been made thirty years ago, by Geuther, concerning the transformation of rose-coloured manganese sulphide into the green modification (*Jena Zeits. f. Med. u. Natur.*, ii., p. 127), and, although it has been subsequently contradicted, we have verified its accuracy. To succeed in this experiment we must place ourselves in conditions analogous to those in which the transformation of zinc sulphide is most readily effected. We take a solution of a salt of manganese, *e.g.*, the chloride, very dilute so that the congelation may be as complete as possible, and precipitate it with a very slight excess of ammonium hydrosulphate. The liquid being frozen, and kept at some degrees below zero, the transformation is effected in a complete manner within twenty-four hours.

We may remark that in the same media the same transformation can only be effected by the action of heat at a temperature above 300°.

Copper Hydroxide. — Copper hydroxide is known in various states. If precipitated by an alkali from the solution of a salt of copper, such as the sulphate, it is amorphous, of a blue colour slightly mixed with green, and very unstable. Under conditions which have been studied by several chemists, and especially by D. Tommasi (*Bull. Soc. Chimique*, 1882, xxxvii., p. 197), and to which we shall return, it is transformed into the black oxide.

But the blue oxide and the black oxide may themselves exist in several states representing different condensations. We shall subsequently study these conditions in which the successive transformations are produced,—conditions similar to those which we have found in studying zinc sulphide. At present we shall restrict ourselves to indicating a transformation of the blue copper sulphide which may be obtained by the foregoing method.

Peligot (*Ann. de Chim. et de Phys.*, Series 3, lxiii., p. 347, 1861), on precipitating, under certain conditions, salts of ammoniacal copper, by an alkali or by water, obtained a copper oxide, $CuOHO$, differing from the ordinary blue oxide by its crystalline state, its beautiful turquoise-blue colour, and its very great stability, which render it fit for industrial applications.

This substance may be easily prepared by the transformation of the ordinary hydroxide. If we prepare the latter in the cold by precipitating a solution of copper sulphate not very concentrated, and washing the precipitate with ice-water, the oxide thus obtained presents under the microscope the aspect of a completely amorphous mass having no action upon polarised light. If we freeze the liquid which holds the precipitate in suspension, and keep the temperature below zero, we find that in two hours the crystallisation of the precipitate is much advanced, and the action upon polarised light is very manifest. After several hours the transformation is complete, and the amorphous precipitate is transformed into small dense crystals, presenting the composition and all the characters of Peligot's oxide.

It is probable that some crystalline minerals may thus have been produced by the action of cold. In the course of this investigation we shall find a great number of similar cases.—*Comptes Rendus*, cxx., p. 322.

ACTION OF FLUORINE UPON ARGON.

By HENRI MOISSAN.

The beautiful discovery of argon by Lord Rayleigh and Prof. Ramsay serves to prove that the gaseous bodies, as well as the solids which we encounter in Nature, may contain in very small quantities elements hitherto overlooked. This gas argon presents further a character quite special, for its chemical activity is almost *nil*. Its physical properties have permitted its detection, its preparation, and its study.

Prof. Ramsay, having had the kindness to give me 100 c.c. of this argon, to endeavour to combine it with fluorine, I have been able to perform upon this new gas some experiments which I shall briefly describe.

For some years I have taken occasion to study several simple substances which, under given conditions of temperature, combine with nitrogen very energetically. Such are especially boron and titanium.

I heated titanium, as pure as possible, in an atmosphere of argon, to the temperature at which ordinary glass softens. After heating for thirty minutes there was no decrease of volume, and consequently no probable combination. The titanium had not changed in its appearance.

Pure boron, prepared by means of magnesium heated in a bell of Bohemian glass, did not combine with argon, whilst under the same conditions it united with nitrogen, forming solid boron nitride.

This argon, heated in presence of lithium, does not decrease in volume, yet it is known that under this condition nitrogen rapidly yields a solid lithium nitride, as M. Ouvrard has demonstrated (*Compt. Rend.*, cxiv., p. 120).

The curious decomposition of clèveite by sulphuric acid led me to examine if uranium had any action upon argon. A volume of argon, measured at the mercurial trough, was heated in a small bent tube of common glass along with several fragments of uranium. After heating for twenty minutes the volume of gas was not modified. The uranium had been prepared in the electric furnace, and contained 3·5 per cent of carbon.

To study the action of fluorine upon this new simple substance I made use of the following apparatus:—

A cylinder of platinum, of 10 c.m. in length and 2 c.m. in diameter, is closed by two metallic supports holding discs of transparent fluor-spar with parallel surfaces. On the sides there enter two small tubes of platinum, the one conveying fluorine and the other argon. These two tubes open opposite to each other. A third tube, placed at the end of the cylinder, allows the gaseous mixture to escape. Small metal cocks enable the apparatus to be closed without being able to exert a strong pressure. Lastly, a metallic rod, insulated by the transparent plate of fluor-spar which it traverses, allows the spark of an induction coil to be made to strike in the interior.

The metal supports which contain the discs of transparent fluor-spar, as also the ends of the tubes, are tightened by means of screws which crush upon a small ring of lead placed at the edge of the two tubes to be connected.

The platinum cylinder, dried with care, which had served for preparing pure fluorine, and which has been described (*Annales de Chimie et de Physique*, Series 6, xxiii.), was placed at the end of the apparatus.

All the air of the apparatus was swept out by passing through it 3 or 4 litres of fluorine. The gas which was liberated occasioned no fume in the air, and gave a lively incandescence with silicon. The current of fluorine was stopped, and the argon was introduced through the other platinum tube, being gently displaced by mercury in a small bell fitted with a cock. When the very slow current of argon gas arrived into the fluorine no visible phenomenon was produced. On holding the tube in the fingers no change of temperature was felt.

The electric spark was made to strike into this mixture of argon and fluorine, but it produced no apparent reaction.

The experiment was re-commenced twice, so as to vary the proportions of argon, and the results were still negative.

The difficulty of manipulating fluorine did not allow us to try if a change of volume might ultimately ensue by the action of a series of sparks.

The conclusion which we draw from these experiments is, that at the ordinary temperature, or under the action of the induction spark, a mixture of fluorine and argon does not enter into combination.—*Comptes Rendus*, cxx., p. 966.

THE ACTION OF HEAT UPON ETHYLENE.*
II.

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.
(Concluded from p. 287).

Some information can be obtained as to the secondary reactions which accompany the main decomposition by studying the proportions in which the products, other than ethylene, are present in the gases after heating.

Taking the experiments made upon the effect of length of heated tube and rate of flow, and tabulating the percentages of saturated hydrocarbons and hydrogen corrected for change of volume, we obtain the following results:—

Saturated Hydrocarbons.

Length of tube heated.	1 inch.	6 inches.	18 inches.
5 c.c.	43·72	63·42	70·13
15 c.c.	38·02	44·44	60·46
40 c.c.	25·12	39·16	55·37

The temperature employed in these experiments is not sufficiently high to cause any large amount of the methane to decompose, so that the volume should, according to theory, approximate to two-thirds of the ethylene decomposed.

Rate of flow per minute.	Ethylene decomposed.	Methane found.	Calculated.	Variation.
		1 inch of heated tube.		
5 c.c.	80·10	43·72	53·40	−9·68
15 ,,	70·83	38·02	47·22	−9·20
40 ,,	50·58	25·12	33·72	−8·60
		6 inches of heated tube.		
5 c.c.	85·48	63·42	56·98	+6·44
15 ,,	79·42	44·44	52·94	−8·50
40 ,,	63·17	39·16	42·12	+2·96
		18 inches of heated tube.		
5 c.c.	93·76	70·13	64·50	+5·63
15 ,,	90·31	60·46	60·20	+0·26
40 ,,	87·15	55·37	58·10	−2·73

The fact that when only 1 in. of tube is heated there is a fairly constant deficit of the kind to be expected at the temperature employed, and that when a greater length of heated tube is used with a 5 c.c. rate of flow, the deficit becomes a substantial surplus, at once suggests that methane is amongst the secondary as well as the primary products of decomposition.

In the dilution experiments, the larger contraction in the volume noticeable points to the diluting of the products favouring polymerisation.

Dilution.	Ethylene decomposed.	Methane.		Variation.
		Found.	Calculated.	
Nil	72·27	40·85	48·18	−7·33
10 per cent ..	66·84	35·27	44·56	−9·29
25 ,, ..	53·85	33·43	35·90	−2·47
50 ,, ..	34·88	23·04	23·24	−0·20
75 ,, ..	15·15	13·43	10·10	+3·33
95 ,, ..	2·89	4·85	1·92	+2·93

And it seems probable from the figures that when dilution reaches above 50 per cent, not only is decomposition of the methane retarded, but formation as a secondary product commences.

Ever since water gas has been in use it has been well known that it contained traces of methane and acetylene, under conditions which render it impossible for them to have been formed from hydrocarbons remaining in the incandescent fuel, and the probabilities are that they have been produced, the acetylene by direct combination of carbon and hydrogen, and the methane by its partial decomposition.

The formation of ethylene from nascent hydrogen and acetylene takes place at such temperatures as those employed, and the amount so formed and again broken up by the radiant heat is purely a function of mass; so that I conceive from these experiments, the ethylene at once to a great extent decomposes under the influence of sufficiently high radiant heat according to the equation—

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$

and that the acetylene partly decomposes, the nascent hydrogen again uniting with more acetylene to reproduce ethylene, whilst other portions of the acetylene polymerise to benzene and other more complex hydrocarbons, and that, if the flow of this mixture be continued through a heated chamber, the action continues, the amount of ethylene regenerated becoming less and less, until it ceases to exist as a product of the decomposition.

It is well known that hydrogen will diffuse through ignited platinum into a vacuous space or even into other gases, and although no change in volume was observed when a mixture of 95 per cent hydrogen and 5 per cent ethylene was passed through the tube heated to 900° C.,

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* A Paper read before the Royal Society.

it seemed advisable to make special experiments to ascertain if any loss of hydrogen from this cause did take place at the temperature employed.

The apparatus having been fitted up as before, 6 in. of the tube were heated to between 900° and 1000° C., and a carefully measured volume of pure hydrogen was made to pass through it three times at a slow rate of flow, with the result that, after being brought back to its original temperature and pressure, it measured 99·5 per cent of the volume taken, showing that error from this cause is not likely to have taken place.

A new series of experiments was now undertaken to ascertain, if possible, how increase of contact with the heated walls of the containing vessel affected the amount and character of the decomposition taking place.

In order to do this, a small platinum tube, 2·5 m.m. in diameter and 45·72 c.m. long was taken in place of the one used in the previous experiments, which was 14 m.m. in diameter. The area of the big tube therefore, as compared with the area of the small tube, was as 1·54 to 0·049, and in order to obtain the relative amount of decomposition it is manifest that the rate of flow must be the same in both tubes.

If the rate of flow in the big tube be 40 c.c. per minute, then—

$$\frac{2{\cdot}5^2 \times 40}{14^2} = 1{\cdot}27$$

will give the required rate for the small tube.

Table V.

Temperature, 900° C. Rate of Flow, 1·27 c.c. per min.

Length of tube heated.	1 inch.		6 inches.		12 inches.	
Volume of gas—						
Before heating..	100		100		100	
After heating ..	80		91		97	
Analysis of Gaseous Products.						
Carbon dioxide ..	1·00		0·75		0·75	
Oxygen..	0·25		0·00		0·25	
*Unsaturated hydrocarbons ..	15·30		12·20		6·30	
Carbon monoxide	0·75		1·00		1·00	
Saturated hydrocarbs. by absorp.	13·50	50·50	12·10	60·30	9·50	54·50
Do. by explos.	37·00		48·20		45·00	
Hydrogen	26·00		18·75		30·80	
Nitrogen	6·20		7·00		6·40	
*Containing acetylene	0·3		0·32		0·20	

Correcting the unsaturated hydrocarbons for change in volume, we obtain undecomposed—

I.	II.	III.
12·00	10·81	5·92

The ethylene used contained 96·75 per cent of unsaturated hydrocarbons; therefore the amount decomposed is—

I.	II.	III.
84·75	85·94	90·83

Turning now to the experiments made with the large tube and 40 c.c. a minute rate of flow, we find that the percentage of ethylene decomposed was—

I. 1 inch.	II. 6 inches.	III. 12 inches.
50·58	63·17	75·16 calctd.

an increase of decomposition with the small tube amounting to the following percentages:—

I.	II.	III.
33·93	22·48	15·48

showing that the maximum increase of 34 per cent rapidly falls with increased length of flow, whilst the ratio of area of heated surface to the passing gas is 43·96/7·85, or 5·6 times as great in the small tube as in the large, yet only gives an increase of one-third at most in the decomposition.

From the results of these experiments it may be stated that—

1. The initial decomposition of ethylene by heat is very rapid, and requires but a short flow through a heated containing vessel, such primary decomposition, however, being but slowly completed, owing to secondary reactions, which tend to reform ethylene.
2. Dilution has but little effect in retarding the decomposition of ethylene, unless it be very large.
3. Increase in rate of flow diminishes the amount of decomposition when the heated area is small, but rapidly diminishes in effect as the length of flow through a heated area increases.
4. The decomposition of ethylene is chiefly caused by radiant heat, the effect of which is very great as compared with the decomposition due to contact with heated surfaces.

I desire to acknowledge the valuable aid given me by Mr. F. B. Grundy in this investigation.

ARGON.[*]

By the Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D., F.R.S., Professor of Natural Philosophy, R.I.

It is some three or four years since I had the honour of lecturing here one Friday evening upon the densities of oxygen and hydrogen gases, and upon the conclusions that might be drawn from the results. It is not necessary, therefore, that I should trouble you to-night with any detail as to the method by which gases can be accurately weighed. I must take that as known, merely mentioning that it is substantially the same as is used by all investigators nowadays, and introduced more than fifty years ago by Regnault. It was not until after that lecture that I turned my attention to nitrogen; and in the first instance I employed a method of preparing the gas which originated with Mr. Vernon Harcourt, of Oxford. In this method the oxygen of ordinary atmospheric air is got rid of with the aid of ammonia. Air is bubbled through liquid ammonia, and then passed through a red-hot tube. In its passage the oxygen of the air combines with the hydrogen of the ammonia, all the oxygen being in that way burnt up and converted into water. The excess of ammonia is subsequently absorbed with acid, and the water by ordinary desiccating agents. That method is very convenient; and, when I had obtained a few concordant results by means of it, I thought that the work was complete, and that the weight of nitrogen was satisfactorily determined. But then I reflected that it is always advisable to employ more than one method, and that the method that I had used—Mr. Vernon Harcourt's method—was not that which had been used by any of those who had preceded me in weighing nitrogen. The usual method consists in absorbing the oxygen of air by means of red-hot copper; and I thought that I ought at least to give that method a trial, fully expecting to obtain forthwith a value in harmony with that already afforded by the ammonia method. The result, however, proved otherwise. The gas obtained by the copper method, as I may call it, proved to be one-thousandth part heavier than that obtained by the ammonia method; and, on repetition, that difference was only brought out more clearly. This was about three years ago. Then, in order, if possible, to get further light upon a discrepancy which puzzled me very much, and which, at that time, I regarded only with disgust and impatience, I published a letter in *Nature* inviting criticisms from chemists who

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[*] A Lecture delivered at the Royal Institution of Great Britain Friday, April 5, 1895.

might be interested in such questions. I obtained various useful suggestions, but none going to the root of the matter. Several persons who wrote to me privately were inclined to think that the explanation was to be sought in a partial dissociation of the nitrogen derived from ammonia. For, before going further, I ought to explain that, in the nitrogen obtained by the ammonia method, some—about a seventh part—is derived from the ammonia, the larger part, however, being derived as usual from the atmosphere. If the chemically-derived nitrogen were partly dissociated into its component atoms, then the lightness of the gas so prepared would be explained.

The next step in the enquiry was, if possible, to exaggerate the discrepancy. One's instinct at first is to try to get rid of a discrepancy; but I believe that experience shows such an endeavour to be a mistake. What one ought to do is to magnify a small discrepancy with a view to finding out the explanation; and, as it appeared in the present case that the root of the discrepancy lay in the fact that part of the nitrogen prepared by the ammonia method was nitrogen out of ammonia, although the greater part remained of common origin in both cases, the application of the principle suggested a trial of the weight of nitrogen obtained wholly from ammonia. This could easily be done by substituting pure oxygen for atmospheric air in the ammonia method, so that the whole, instead of only a part, of the nitrogen collected should be derived from the ammonia itself. The discrepancy was at once magnified some five times. The nitrogen so obtained from ammonia proved to be about one-half per cent lighter than nitrogen obtained in the ordinary way from the atmosphere, and which I may call for brevity "atmospheric" nitrogen.

That result stood out pretty sharply from the first; but it was necessary to confirm it by comparison with nitrogen chemically derived in other ways. The table before you gives a summary of such results, the numbers being the weights in grms. actually contained under standard conditions in the globe employed :—

Atmospheric Nitrogen.	
By hot copper (1892)	2·3103
By hot iron (1893)	2·3100
By ferrous hydrate (1894)	2·3102
Mean	2·3102
Chemical Nitrogen.	
From nitric oxide	2·3001
From nitrous oxide	2·2990
From ammonium nitrite purified at a red-heat	2·2987
From urea	2·2985
From ammonium nitrite purified in the cold	2·2987
Mean	2·2990

The difference is about 11 m.grms., or about one-half per cent; and it was sufficient to prove conclusively that the two kinds of nitrogen—the chemically-derived nitrogen and the atmospheric nitrogen—differed in weight, and therefore, of course, in quality, for some reason hitherto unknown.

I need not spend time in explaining the various precautions that were necessary in order to establish surely that conclusion. One had to be on one's guard against impurities, especially against the presence of hydrogen, which might seriously lighten any gas in which it was contained. I believe, however, that the precautions taken were sufficient to exclude all questions of that sort, and the result, which I published about this time last year, stood sharply out, that the nitrogen obtained from chemical sources was different from the nitrogen obtained from the air.

Well, that difference, admitting it to be established, was sufficient to show that some hitherto unknown gas is involved in the matter. It might be that the new gas was dissociated nitrogen, contained in that which was too light, the chemical nitrogen,—and at first that was the explanation to which I leaned; but certain experiments went a long way to discourage such a supposition. In the first place, chemical evidence—and in this matter I am greatly dependent upon the kindness of chemical friends—tends to show that, even if ordinary nitrogen could be dissociated at all into its component atoms, such atoms would not be likely to enjoy any very long-continued existence. Even ozone goes slowly back to the more normal state of oxygen; and it was thought that dissociated nitrogen would have even a greater tendency to revert to the normal condition. The experiment suggested by that remark was as follows :—to keep chemical nitrogen—the too light nitrogen which might be supposed to contain dissociated molecules—for a good while, and to examine whether it changed in density. Of course it would be useless to shut up gas in a globe and weigh it, and then, after an interval, to weigh it again, for there would be no opportunity for any change of weight to occur, even although the gas within the globe had undergone some chemical alteration. It is necessary to re-establish the standard conditions of temperature and pressure which are always understood when we speak of filling a globe with gas, for I need hardly say that filling a globe with gas is but a figure of speech. Everything depends upon the temperature and pressure at which you work. However, that obvious point being borne in mind, it was proved by experiment that the gas did not change in weight by standing for eight months—a result tending to show that the abnormal lightness was not the consequence of dissociation.

Further experiments were tried upon the action of the silent electric discharge,—both upon the atmospheric nitrogen and upon the chemically-derived nitrogen, but neither of them seemed to be sensibly affected by such treatment; so that, altogether, the balance of evidence seemed to incline against the hypothesis of abnormal lightness in the chemically-derived nitrogen being due to dissociation, and to suggest strongly, as almost the only possible alternative, that there must be in atmospheric nitrogen some constituent heavier than true nitrogen.

At that point the question arose, What was the evidence that all the so-called nitrogen of the atmosphere was of one quality? And I remember—I think it was about this time last year, or a little earlier—putting the question to my colleague, Professor Dewar. His answer was that he doubted whether anything material had been done upon the matter since the time of Cavendish, and that I had better refer to Cavendish's original paper. That advice I quickly followed, and I was rather surprised to find that Cavendish had himself put this question quite as sharply as I could put it. Translated from the old-fashioned phraseology connected with the theory of phlogiston, his question was whether the inert ingredient of the air is really all of one kind; whether all the nitrogen of the air is really the same as the nitrogen of nitre. Cavendish not only asked himself this question, but he endeavoured to answer it by an appeal to experiment.

I should like to show you Cavendish's experiment in something like its original form. He inverted a U-tube filled with mercury, the legs standing in two separate mercury cups. He then passed up, so as to stand above the mercury, a mixture of nitrogen, or of air, and oxygen; and he caused an electric current from a frictional electrical machine, like the one I have before me, to pass from the mercury in the one leg to the mercury in the other, giving sparks across the intervening column of air. I do not propose to use a frictional machine to-night, but I will substitute for it one giving electricity of the same quality of the construction introduced by Mr. Wimshurst, of which we have a fine specimen in the Institution. It stands just outside the door of the theatre, and will supply an electric current along insulated wires, leading to the mercury cups; and, if we are successful, we shall cause sparks to pass through the small length of air included above the columns of mercury. There they are; and after a little time you will notice that the mercury rises, indicating that the gas is sensibly absorbed under the influence of the sparks and of a piece of potash floating on the mercury. It was by that means that Cavendish established his great discovery of the nature of the inert ingredient in the atmosphere, which we now call nitrogen; and, as I have said, Cavendish himself proposed the question, as distinctly as we can do, Is this inert ingredient all of one kind? and he proceeded to test that question. He found, after days and weeks of protracted experiment, that, for the most part, the nitrogen of the atmosphere was absorbed in this manner, and converted into nitrous acid; but that there was a small residue remaining after prolonged treatment with sparks, and a final absorption of the residual oxygen. That residue amounted to about $\frac{1}{120}$th part of the nitrogen taken; and Cavendish draws the conclusion that, if there be more than one inert ingredient in the atmosphere, at any rate the second ingredient is not contained to a greater extent than $\frac{1}{120}$th part.

I must not wait too long over the experiment. Mr. Gordon tells me that a certain amount of contraction has already occurred; and if we project the U upon the screen, we shall be able to verify the fact. It is only a question of time for the greater part of the gas to be taken up, as we have proved by preliminary experiments.

In what I have to say from this point onwards, I must be understood as speaking as much on behalf of Professor Ramsay as for myself. At the first, the work which we did was to a certain extent independent. Afterwards we worked in concert, and all that we have published in our joint names must be regarded as being equally the work of both of us. But, of course, Professor Ramsay must not be held responsible for any chemical blunder into which I may stumble to-night.

By his work and by mine the heavier ingredient in atmospheric nitrogen which was the origin of the discrepancy in the densities has been isolated, and we have given it the name of "argon." For this purpose we may use the original method of Cavendish, with the advantages of modern appliances. We can procure more powerful electric sparks than any which Cavendish could command by the use of the ordinary Ruhmkorff coil stimulated by a battery of Grove cells; and it is possible so to obtain evidence of the existence of argon. The oxidation of nitrogen by that method goes on pretty quickly. If you put some ordinary air, or, better still, a mixture of air and oxygen, in a tube in which electric sparks are made to pass for a certain time, then in looking through the tube, you observe the well-known reddish orange fumes of the oxides of nitrogen. I will not take up time in going through the experiment, but will merely exhibit a tube already prepared (image on screen),

One can work more efficiently by employing the alternate currents from dynamo machines which are now at our command. In this Institution we have the advantage of a public supply; and if I pass alternate currents originating in Deptford through this Ruhmkorff coil, which acts as what is now called a "high potential transformer," and allow sparks from the secondary to pass in an inverted test-tube between platinum points, we shall be able to show in a comparatively short time a pretty rapid absorption of the gases. The electric current is led into the working chamber through bent glass tubes containing mercury, and provided at their inner extremities with platinum points. In this arrangement we avoid the risk, which would otherwise be serious, of a fracture just when we least desired it. I now start the sparks by switching on the Ruhmkorff to the alternate current supply; and, if you will take note of the level of the liquid representing the quantity of mixed gases included, I think you will see after, perhaps, a quarter of an hour that the liquid has very appreciably risen, owing to the union of the nitrogen and the oxygen gases under the influence of the electrical discharge, and subsequent absorption of the resulting compound by the alkaline liquid with which the gas space is enclosed.

By means of this little apparatus, which is very convenient for operations upon a moderate scale, such as for analyses of "nitrogen" for the amount of argon that it may contain, we are able to get an absorption of about 80 c.c. per hour, or about 4 inches along this test-tube, when all is going well. In order, however, to obtain the isolation of argon on any considerable scale by means of the oxygen method, we must employ an apparatus still more enlarged. The isolation of argon requires the removal of nitrogen, and, indeed, of very large quantities of nitrogen, for, as it appears, the proportion of argon contained in atmospheric nitrogen is only about 1 per cent, so that for every litre of argon that you wish to get you must eat up some hundred litres of nitrogen. That, however, can be done upon an adequate scale by calling to our aid the powerful electric discharge now obtainable by means of the alternate current supply and high potential transformers.

In what I have done upon this subject I have had the advantage of the advice of Mr. Crookes, who some years ago drew special attention to the electric discharge or flame, and showed that many of its properties depended on the fact that it had the power of causing, upon a very considerable scale, a combination of the nitrogen and the oxygen of the air in which it was made.

I had first thought of showing in the lecture-room the actual apparatus which I have employed for the concentration of argon; but the difficulty is that, as the apparatus has to be used, the working parts are almost invisible, and I came to the conclusion that it would really be more instructive as well as more convenient to show the parts isolated, a very little effort of imagination being then all that is required in order to reconstruct in the mind the actual arrangements employed.

First, as to the electric arc or flame itself. We have here a transformer made by Pike and Harris. It is not the one that I have used in practice; but it is convenient for certain purposes, and it can be connected by means of a switch with the alternate currents of 100 volts furnished by the Supply Company. The platinum terminals that you see here are modelled exactly upon the plan of those which have been employed in practice. I may say a word or two on the question of mounting. The terminals require to be very massive on account of the heat evolved. In this case they consist of platinum wire doubled upon itself six times. The platinums are continued by iron wires going through glass tubes, and attached at the ends to the copper leads. For better security, the tubes themselves are stopped at the lower ends with corks and charged with water, the advantage being that, when the whole arrangement is fitted by means of an indiarubber stopper into a closed vessel, you have a witness that, as long as the water remains in position, no leak can have occurred through the insulating tubes conveying the electrodes.

Now, if we switch on the current and approximate the points sufficiently, we get the electric flame. There you have it. It is, at present, showing a certain amount of soda. That in time would burn off. After the arc has once been struck, the platinums can be separated; and then you have two tongues of fire ascending almost independently of one another, but meeting above. Under the influence of such a flame, the oxygen and the nitrogen of the air combine at a reasonable rate, and in this way the nitrogen is got rid of. It is now only a question of boxing up the gas in a closed space, where the argon concentrated by the combustion of the nitrogen can be collected. But there are difficulties to be encountered here. One cannot well use anything but a glass vessel. There is hardly any metal available that will withstand the action of strong caustic alkali and of the nitrous fumes resulting from the flame. One is practically limited to glass. The glass vessel employed is a large flask with a single neck, about half full of caustic alkali. The electrodes are carried through the neck by means of an india-rubber bung provided also with tubes for leading in the gas. The electric flame is situated at a distance of only about half an inch above the caustic alkali. In that way an efficient circulation is established; the hot gases as they rise from the flame strike the top, and then as they come round again in the course of the circulation they pass sufficiently close to the caustic alkali to ensure an adequate removal of the nitrous fumes.

There is another point to be mentioned. It is necessary to keep the vessel cool; otherwise the heat would soon rise to such a point that there would be excessive generation of steam, and then the operation would come to a standstill. In order to meet this difficulty the upper part of the vessel is provided with a water-jacket, in which a circulation can be established. No doubt the glass is severely treated, but it seems to stand it in a fairly amiable manner.

By means of an arrangement of this kind, taking nearly three horse-power from the electric supply, it is possible to consume nitrogen at a reasonable rate. The transformers actually used are the "Hedgehog" transformers of Mr. Swinburne, intended to transform from 100 volts to 2400 volts. By Mr. Swinburne's advice I have used two such, the fine wires being in series so as to accumulate the electrical potential and the thick wires in parallel. The rate at which the mixed gases are absorbed is about 7 litres per hour; and the apparatus, when once fairly started, works very well as a rule, going for many hours without attention. At times the arc has a trick of going out, and it then requires to be re-started by approximating the platinums. We have already worked fourteen hours on end, and by the aid of one or two automatic appliances it would, I think, be possible to continue operations day and night.

The gases, air and oxygen in about equal proportions, are mixed in a large gasholder, and are fed in automatically as required. The argon gradually accumulates; and when it is desired to stop operations the supply of nitrogen is cut off, and only pure oxygen allowed admittance. In this way the remaining nitrogen is consumed, so that, finally, the working vessel is charged with a mixture of argon and oxygen only, from which the oxygen is removed by ordinary well-known chemical methods. I may mention that at the close of the operation, when the nitrogen is all gone, the arc changes its appearance, and becomes of a brilliant blue colour.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

THE CONVERSAZIONE AT THE ROYAL SOCIETY.

June 12th, 1895.

Among the articles exhibited and the procedures shown at this Converzazione there were not a few which must exceptionally appeal to readers of the Chemical News.

Thus, in Room No. 1 (the office) we noticed an electrograph for indelible linen marking. The linen is moistened with a saline solution, or in default with plain water, and a current is passed for about two minutes from a silver die, thus conveying silver into the fibres wherever the die touches. On reversing the current for three seconds, the silver thus deposited in the tissue is reduced, fixed in the metallic state. We believe that an analogous process has been successfully applied in certain styles in tissue-printing.

In Room 2 (the Reception Room) Dr. Gladstone, F.R.S., exhibited photographs of curvilinear crystals of water and specimens of curvilinear crystals of soda salts. The scientific importance of this exhibit is of great moment: it was formerly maintained that only organic bodies, *e.g.*, animals and plants or their parts, can solidify in curvilinear figures. The only familiar exception to this rule, the diamond, was explained as being pre-eminently *the* organic element.

In Room No. 3 (the Council Room), Mr. W. Gowland exhibited Japanese pictures as showing the effects of time on the pigments used by Japanese artists from A.D. 1322 to the beginning of the present century. For greens and blues these painters used copper carbonate; for a permanent blue, *Lapis lazuli*, *i.e.*, natural ultramarine. For reds, ferric oxide, vermilion, and carmine; for permanent white, levigated oyster shells; and for a black, a lamp-black from the oil of *Sesamum indicum*.

Prof. Roberts-Austen, C.B., F.R.S., exhibited the electrical furnace used for obtaining carbon in the diamond state and for fusing chromium, titanium, platinum, and others of the most refractory metals. The furnace has a fire-clay case lined with magnesia, and the crucibles used are of magnesia. The carbon poles lie horizontally, and the arc is deflected upon the material to be heated by means of a magnet. In exhibiting the process, an image of the melted contents of the furnace is thrown upon a screen by means of a lens and mirror. The current used was from 60 to 70 ampères and 100 volts. This exhibition was strikingly satisfactory.

In Room 4 (Principal Library), Mr. J. Norman Lockyer, C.B., F.R.S., showed photographs of apparatus used for collecting the gases obtained from various minerals by the distillatory method. The small retort containing the specimen is attached end-wise to a spectrum tube joined to a Sprengel pump. After exhaustion, the mineral is heated to redness and the spectra of the gases emitted at different stages are observed in the spectrum tube and photographed.

The same *savant* exhibits also photographs of the spectra of Bellatrix, and of a part of the sun's atmosphere. Here are seen coincidences with the lines as photographed in the spectra of the gases evolved from uraninite. It is remarked that "we appear to be in presence of the *vera causa* of many of the lines hitherto classed as unknown."

A further exhibition shows the spectra of the rare gases:—

(*a*) Presence of the yellow line D_3; in some cases with the blue line 4471, and in others without it.

(*b*) Presence of yellow line with the ultra-violet line 3889, and in other cases without it.

A set of experiments showing inversions in the intensities of lines appearing in the spectra of the new gas from uraninite.

In the same room, Mr. W. F. H. Blandford showed specimens illustrating chromogeny in South American butterflies, interesting both to the chemist and the biologist.

Mr. W. T. Burgess exhibited experiments demonstrating the conveyance of infection by flies. The part played by these insects in the diffusion of pathogenic microbia is now placed beyond all doubt.

Prof. Marshall Ward, F.R.S., exhibited a series of cultures of bacteria isolated from the water of the Thames. Some of these are still unknown.

The Marine Biological Association showed the method of fixing methylene-blue preparations by means of ammonium molybdate, as invented by Dr. Barthe, of Berlin.

Prof. A. Liversidge, F.R.S., exhibits sectioned of gold nuggets etched to show their crystalline structure. The designs brought out on slicing, polishing, and etching with chlorine-water resemble the well-known Widmanstatt figures, but are more or less square in section.

Prof. Ramsay, F.R.S., exhibited spectra of argon and of helium mixed with argon. A sodium flame is shown to prove the non-identity of the D_3 line of helium with the sodium D_1 and D_2 lines.

PHYSICAL SOCIETY.

Ordinary Meeting, June 14th, 1895.

Captain W. de W. Abney, President, in the Chair.

Mr. Burstall continued the reading of his paper "*On the Measurement of Cyclically varying Temperature.*"

Three sizes of platinum wire have been employed for the thermometers, in order that some idea might be formed as to the magnitude of the error caused by the lag of the temperature of the wire behind that of the gases. The constants of the platinum thermometers were determined either by comparison with a standard Callendar platinum thermometer, or by means of ice, boiling water, and boiling sulphur. In most cases the thermometer constants were determined after the wire had been exposed to the action of the hot gases for about half an hour. One wire, however, was calibrated before being used, and an unusually high value was obtained for the coefficient δ. After this wire had been exposed to the hot gases, the value of δ fell, however, to the normal. The author thinks the abnormal value may have been due to the formation of a gold-platinum alloy during the process of attaching the wire to the leads, and that this alloy was subsequently swept off by the hot gases.

The paper includes a number of tables and curves which embody the numerical results, and show that concordant results can be obtained on different days and with different thermometers.

Prof. Perry said that an instrument for quickly recording varying temperatures was greatly required by engineers. The temperature just inside the cylinder-walls was, however, most important to determine; and a knowledge of how the temperature from 1 to 2 m.m. inside the walls varied would be of the greatest value. He would like to ask the author if the observed temperatures agreed with the values calculated on the assumption that the gases in the cylinder behaved as a perfect gas, and that—

$$\frac{PV}{T} = \text{constant}$$

during the whole stroke. Differences between the observed and calculated values might be due to dissociation, and not entirely to lag in the thermometers. It was astonishing that even the fine wires employed were able to follow the rapidly varying temperature, and he would like to see some special experiments made to test this point.

Prof. Capper showed a diagram giving the values calculated on the assumption that—

$$\frac{PV}{T} = \text{constant.}$$

In such a calculation it was necessary to assume some temperature as a starting point, and in general this temperature was obtained from an analysis of the exhaust gases, so that the calculated curve is most likely to depart from the truth at the commencement of the stroke. He (Prof. Capper) hoped that the author would be able to accurately determine the temperature of some one point of the stroke, and he suggested that the point where the observed curve crossed the theoretical curve would be the most suitable one for this purpose. Such a point must exist, since at the commencement of the stroke the lag causes the observed temperature to be too low, while at the end of the stroke the observed temperatures are too high. Mr. Burstall finds a curious bump in his curves, and it is curious that a similar bump exists in the calculated curves. From the constancy with which this bump appears, it would seem that it must have some physical meaning. It was important to remember that the expansion of the gas-engine cylinder is not adiabatic, for heat is both abstracted and generated during the stroke.

Mr. Blakesley suggested that since the temperatures dealt with were sufficient to make the wire red-hot, the question of lag might be investigated by means of Becquerel's phosphoroscope at a known interval after the removal of the source of heat.

Mr. Griffiths said he considered an important source of error was the large thermal capacity of the leads when the working wire was so very short. He thought it would be possible to standardise the thermometers under conditions somewhat similar to those which occur in the engine cylinder. Thus, perhaps alternate gushes of air at 0° and 100° C. might be used. The use of gold to attach the fine wire to the leads was objectionable, since the gold must permeate the platinum for quite an appreciable fraction of the whole length of the wire. He would like to know whether the change in δ alluded to by the author occurred with the first explosion or whether it was a gradual one.

Mr. Enright pointed out that the nature of the working substance in a gas-engine varied during the stroke.

Prof. Perry said that the change in the specific volume of the gases before and after combustion did not amount to more than 1·25 per cent.

Mr. E. Wilson said he thought it was most important to shorten the time of contact, since at present the galvanometer readings corresponded to the mean temperature over a range of about 5 per cent of the whole stroke. It might be possible to make use of a condenser to get over this difficulty.

Prof. Rücker said that the Kew Observatory were making arrangements to undertake the testing of platinum thermometers.

Mr. Enright suggested that with a very short contact induced currents might cause errors.

Mr. Rhodes said that he had found that the method of determining the zero-point of thermometers, by means of melting ice, was far from satisfactory, and that the results obtained could not be depended upon to within 0·1° C.

The author, in his reply, said the only chemical action on the wires he thought probable was the formation of a carbide. After several hours use, however, the wires appear quite bright and clean.

Mr. N. F. Deerr read a paper on "*The Thermal Constants of the Elements.*"

The object of the paper is to establish the following laws:—If T denote the melting-point on the absolute scale, C the mean coefficient of expansion between zero and the melting-point, S the mean specific heat, and L the latent heat of fusion, then, for any family in Mendeleeff's periodic classification, the following relations will hold between metals and metals, and between non-metals and non-metals:—

$$\left(T + \frac{L}{S}\right) C = \text{const.}$$

$$TC = \text{const.}$$

$$\frac{LC}{S} = \text{const.}$$

In the absence of other data the mean values of C and S between 0° and 100° have been taken.

Anomalous values are obtained in the case of gold and mercury, if these metals are included in their usual positions. The author considers that the thermal constants indicate that gold ought to be placed among the transition elements. He further proposes to place mercury in a new group to come before the lithium group. Such a group, he suggests, would at present contain hydrogen, argon, and mercury.

The paper concludes with an attempt to justify the expression—

$$\left(T + \frac{L}{S}\right) C = \text{const.}$$

on theoretical grounds.

Dr. Gladstone considered that the paper contained valuable numerical relationships, and that the second and third formulæ were much more strongly supported by the data given than the first formula. He, the speaker, had also previously noticed that the elements of the transition group might be subdivided into sub-groups, and that the elements of each of these sub-groups were particularly closely related. He agreed with the author that gold ought not to be included in the first group.

Mr. F. H. **Neville** said that since the author did not give the source of the data he had employed, most of the results given were rather indefinite. For example, while the author gives 870° as the melting-point of aluminium, Mr. Haycock and himself had found the value 927°. The value of the latent heat of aluminium given was 29·3, while Pionchon, in a recent paper in the *Comptes Rendus*, gives the value 80. Theoretical considerations appear to indicate that 80 is the minimum value possible. The author assumes that when you heat a substance from the absolute zero to its melting-point, all the energy supplied is employed in the work of expansion. Some of the heat, however, must be employed in changing the kinetic energy of the molecules, even in the case of a solid.

Prof. **Worthington** said that in some cases the amount of work done against cohesive forces between 0° and 100° was much less than one ten-thousandth of the whole amount of energy supplied.

Mr. **Griffiths** said he did not believe in any generalisation which depended on the values of the specific heats determined between 0° and 100°, the rate of change with temperature of specific heat being so great.

The author, in his reply, said he had made every endeavour to obtain the most accurate data for his calculations. The value 29·3 for the latent heat of aluminium was obtained from a paper by J. G. Richards.

A paper on "An Electromagnetic Effect," by Mr. F. W. Bowden, was postponed till the next meeting.

NOTICES OF BOOKS.

Chemical Technology, or Chemistry in its Applications to Arts and Manufactures. Edited by C. E. **Groves**, F.R.S., and W. **Thorp**, B.Sc. With which is incorporated "Richardson and Watt's Chemical Technology," Vol. II., Lighting. 8vo. London: J. and A. Churchill. 1895.

The work before us, if calculated to be very bulky, gives no less a promise of high value or unquestionable excellence. Its successive sections are devoted respectively to fats and oils, by W. Y. Dort; the stearine industry, by J. McArthur; the candle manufacture, by J. and F. A. Field; the petroleum industry and lamps, by Boverton Redwood; and miners' safety-lamps, by B. Redwood and D. A. Louis. No small part of the volume, it will be perceived, treats of matter which pertains to mechanical technology, *i. e.*, the construction of lamps, both for ordinary purposes and for miners' safety-lamps.

In the Introduction we find some hints which may save inventors from mistakes. Thus we are reminded that a room which would be well lighted by means of twenty candles, will be but poorly lighted by means of a single lamp giving light equal to twenty candles. Further, if the flame of such a lamp be surrounded by an opal globe it will be found that the room is better lighted than by the naked flame, though in all probability the globe will intercept one-half of the light.

In the second chapter the delicate question of ascertaining the purity of fats and oils is discussed at considerable length. The after-taste left by mineral and rosin oils at the back of the throat is correctly pronounced a delicate test for such oils.

Maumené's temperature reaction is pronounced valuable in many cases, though, according to Moschini, a previous exposure of the sample to sunlight interferes with the test as far as olive oil is concerned.

The colour-reactions, which were very carefully studied by Calvert and by Chateau, are now considered as of doubtful value, since the reaction, leaving adulterants out of the question, may depend on substances which naturally accompany the oils. They are also modified by the age and condition of the samples, the soil and the climate where they have been produced, and by the degree and method of refining.

The so-called cohesion figures may lead to useful results if the observer has sufficient experience, and if he has at hand pure specimens for comparison.

The absorption spectra enable us to distinguish vegetable oils from those of animal origin. But a very thorough refining is apt to destroy the chlorophyll on which the bands depend.

The use of mineral and rosin oils as adulterants may often be detected by determining the proportion of non-saponifiable oil in the sample.

It is stated that 300,000 tons of Egyptian cotton-seed are now yearly crushed in Britain. It is very satisfactory to learn that the cultivation of the olive is carried on with success in Queensland and South Australia. Of all oils that obtained from olives is most shamelessly sophisticated; some samples sold as fine salad oil are now cotton oil pure and simple.

We do not find here any mention of the new process for obtaining from the cocoa-nut a fatty matter which is probably the best substitute for butter.

Cod-liver oil does not appear to be mentioned, though there is a passing note of its occasional "surrogate," shark-liver oil.

The manufacture of stearine is carefully expounded by J. McArthur, with an account of the three methods of decomposing the neutral fats, viz., saponification with lime or some other base, and decomposition with water alone and with sulphuric acid. The two latter processes are commonly spoken of as saponification.

The candle manufacture is shown by L. and F. A. Field. It is somewhat surprising that, in the very face of the electric light, of gas, and of petroleum lamps, the candle still holds its own. The reason is doubtless its superior simplicity, its convenience, and portability. Nor does it sin so grossly against economy as it is sometimes assumed, since by its means light is obtained where, and only where, it is wanted, whilst gas and the electric light expend much of their energy on the ceiling.

The very rush-light, of course home-made, still sheds its feeble rays in rustic cottages, where at any rate it does not cause explosions.

The night-light is a cheap and useful device of recent times, and is the more to be commended because the fumes of a petroleum lamp when turned down to a mere speck are very anti-sanitary.

The fourth section, on the petroleum industry, by Boverton Redwood, may, both from its extent and its elaborate character, claim the rank of a monograph. We have the history of the mineral oils from a remote antiquity; of the development of petroleum and natural gas industry in the United States, in Russia, in Canada, and in Galicia, as well as in deposits of less importance, including the Assam and Burmese oil-fields.

The geology of petroleum and its origin are next discussed. Mr. Redwood seems disinclined to favour the views of Prof. Mendeleeff; but considers, with Lesley, that the whole mass of animal and vegetable matter in the earth is in the course of successive conversion into light oils, heavy oils, asphalte, and albertite, these changes being accompanied with the liberation of gaseous hydrocarbons.

Incidentally there is a mention of the unfortunate Torbane Hill litigation,—a deplorable affair, since it gave occasion to the enemies of Science to blaspheme. It appears that there exists in New South Wales a deposit resembling in its properties and uses the Scottish Torbane Hill mineral.

Space does not permit us to notice the elaborate account of safety-lamps for mining purposes. One little point, concerning locking and unlocking safety-lamps, we must venture to notice: the motive of the miner for unlocking his lamp is not the desire of obtaining a little more light, but to light his pipe!

It appears that Vol. iii., announced as nearly ready, will also be devoted to means of artificial illumination. The whole work promises, when complete, to be an invaluable library of reference.

CORRESPONDENCE.

THE MOST PROBABLE ATOMIC WEIGHT OF YTTRIUM.

To the Editor of the Chemical News.

Sir,—Since you have kindly reprinted my paper on the atomic weight of yttrium (*Am. Chem. Journ.*, xvii., 154; Chemical News, vol. lxxi., p. 155), I would ask for a little space in your journal to add a word to the letter of Mr. Delafontaine which has appeared on this subject (Chemical News, vol. lxxi., p. 243).

In reference to the historical omissions, it must be said that I have duly cited the work of Mr. Delafontaine, as calculated by Meyer and Seubert in the "Atomgewichte der Elemente" for 1865, and also for 1866.

The determinations of Berlin are quoted neither by Meyer and Seubert, nor by Ostwald in his "Lehrbuch." The original paper of Berlin is not accessible to me, but an abstract (*Berichte*, vi., 1468) states that he found exactly the same value as Clève and Höglund, which, as calculated to-day, is 89·58.

The statement of Mendeleeff in his "Principles of Chemistry" (Translation, p. 88), which gives neither the method of purifying his yttria, nor the method of making the determinations, nor the separate results, can hardly be accepted as the most trustworthy account of the determination of the atomic weight of yttrium; indeed, it is not even referred to by either of the authorities on atomic weights above mentioned.

Coming, now, to the main point—Why has Clève's result been accepted as the most probable? Mr. Delafontaine thinks it is due to Clève's reputation, and because his result fits in with the Periodic System. In matters pertaining to the rarer elements, Clève is indeed a high authority, but what seems to me to be of more importance, is the fact that Clève has worked subsequent to Delafontaine and many others in this field, and has had the benefit of their experience as well as of his own.

The second reason offered does not seem to be very forcible, since chemists are surely not wedded to such an extent to a system in which the inconsistencies are occasionally as striking as the agreements.

Clève's value, as given in Mr. Delafontaine's paper, is 89·7, and it is stated that his yttria was pale yellow. Mr. Delafontaine does not give references to the literature, so that it is difficult to determine just what papers he has in mind. From the latest determinations of Clève (*Bull. Soc. Chim.*, xxxix., 120) it is stated that 23·2091 grms. of yttrium sulphate gave 11·2568 grms. of the oxide, from which, when O = 16 and S = 32·06, yttrium = 89·1. Again, I find no authority for the statement that Clève's yttria was yellow; he claims that the yttria used in his last work was pure, and adds:—"L'yttria pure est parfaitement blanche sans trace de teinte jaune."

It is to be regretted that Mr. Delafontaine does not tell us *why* Clève's results are wrong, rather than end the matter with the statement that they are "evidently inaccurate." It seems to me that the work of Clève has been accepted because it bears internal evidence of its own worth, and not alone for the reasons stated by Mr. Delafontaine. My own results, from yttria purified by Prof. Rowland, leads also to the conclusion that Clève's results are only a little too high.—I am, &c.,

Harry C. Jones.

Chemical Laboratory,
Johns Hopkins University,
June 4, 1895.

REMOVAL OF STOPPERS BY ELECTRICITY.

To the Editor of the Chemical News.

Sir,—Every chemist has experienced the difficulty of removing the glass stopper of a bottle when it has become fixed, apparently immovably. Of course, the best remedy is to heat the neck of the bottle for awhile over a Bunsen burner; the serious drawback, however, of this old-fashioned method lies in the fact that the bottle must be held in horizontal position, and the fluid or solution may be easily spilled out of the bottle if the operation is performed carelessly.

I have solved this little problem in an efficacious, up-to-date, though expensive, manner by rigging up an adjustable clamp with coils of platinum wires embedded in a strip of asbestos attached to the clamp. You press the circular clamp round the neck of the glass bottle, then "press the button, and electricity does the rest."—I am, &c.,

R. W. Hill.

Manchester.

NOTE ON THE
ESTIMATION OF TOTAL ALKALI IN SOAP.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lxxi., p. 285) I have noticed the above inserted as an article of original work by Mr. J. A. Wilson. I cannot see where the originality comes in; he tells us the "determination by difference of free alkali in soap solutions is unreliable, and that he has given up direct titration," at the same time illustrating his remarks in the above note by giving some examples which are only clear to himself.

I should think it would be more interesting if he gave us a new reliable method instead of pointing out errors which are already known. It is all very well to find fault with methods if one can improve them, otherwise it is useless criticising them.—I am, &c.,

P. L. Aslanoglou.

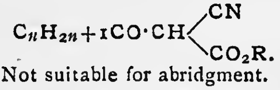
CHEMICAL NOTICES FROM FOREIGN SOURCES

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 22, June 4, 1895.

Volume of Salts in their Aqueous Solutions.—Lecoq de Boisbaudran.—The author holds that it is sometimes advantageous to measure changes of volume by effecting the solution in a dilatometer—an apparatus full of liquids fitted with a graduated stem on which the absolute values of the charges are read off.

Methenic and Methinic Acids.—A Contribution to the Study of the Acetyl-cyanacetic Ethers of the General Formula—



$$C_nH_{2n+1}CO\cdot CH\left<\begin{matrix}CN\\CO_2R.\end{matrix}\right.$$

—A. Haller.—Not suitable for abridgment.

The Specific Gravity of Helium.—Prof. Clève.—Inserted in full.

The Reduction of Nitrous Oxide by Metals in Presence of Water.—Paul Sabatier and J. B. Senderens.

—The results of the authors prove that nitrous oxide in solution is reduced to the state of nitrogen by magnesium, zinc, iron, and even cadmium, with the simultaneous formation of a little ammonia. The gas, on contact with metals moistened with water, dissolves gradually in this water, and is finally reduced in the same manner.

Formation Heat of Sodium Acetylene.—De Forcrand.—The author's results, taking diamond as the form of carbon, appears to be −9·76 cal., whilst for calcium acetylide it was −2·96 cal.

On Phthalyl Chloride and Phthalide.—Paul Rivals.

A Thermo-chemical Investigation.—Conductivity of Certain β-Ketonic Ethers.—J. Guinchant.—The sodium salts of the cyanomethinic acids behave, as concerns their conductivity, in an absolutely normal manner. These acids, like acetyl acetone, obey Ostwald's law (K = const.) as far as it could be expected from compounds containing an acid group and an ether function. For many of these compounds the neutralisation-heat has already been determined, and their chemical affinity deduced from the thermo-chemical measurements agrees with that inferred from the conductivities. For the homologous acids the values of K decrease in proportion as the molecular weight rises.

Determination of Volatile Acids in Wines.—E. Burcker.—The author has found experimentally that the fixed acids, free or combined, exert at most only a negligible action upon the acidity of the distillate, which is due merely to the volatile acids among which the acetic acid takes the principal work. The maximum limit of volatile acidity in sound French wines does not exceed 0·70 grm. per litre, calculated as SO_4H_2. For the wines of Algeria and Tunis it may rise to 1·60 grm. per litre.

Oidium albicans a General Pathogenic Agent.—MM. Chanin and Ostrowsky.—This paper is mainly of medical importance, but it shows that the *Oidium albicans* is a pathogenic agent to be kept in view in sanitary observations. (See Prof. Lehmann, "Methods of Practical Hygiene," translated by W. Crookes, F.R.S., vol. i., p. 159.)

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 5, 1895.

On Natural Dioxystearic Acid.—Paul Juillard.—On saponifying castor oil with caustic soda, the author obtained an isolated or new acid, $C_{18}H_{36}O_4$, an isomer of the acid which he had formerly obtained in alizarene red oils. The acid is insoluble in ether, ligroine, and benzene, scarcely soluble in cold toluene, but more freely if hot; soluble in boiling alcohol and acetic acid. It melts at 141° to 143°. It is a saturated acid of the series $C_nH_{2n}O_4$. It contains two hydroxyls of an alcoholic character, which renders them capable of condensation. According to the manner of treatment it forms two classes of distinct products.

On Triricinoleine, its Ethers and its Synthesis. Artificial Castor Oil.—Paul Juillard.—This synthesis has been effected by heating ricinic acid with glycerin, keeping closely within certain limits of temperature.

On the Constitution of Iodine Green.—Léon Lefèvre.—The iodine green of Hofmann and Girard is an iodomethylate of tetramethyl-triaminodiphenyl cresylmethanol, and not of hexamethyl-triaminodiphenyl cresylmethanol, as certain German *savants* have admitted without proof and without regard to the analysis of Hofmann and Girard. If heated it loses CH_3I, and gives a violet of tetramethyl-triamino-diphenyl cresylmethanol.

Researches on Pectase, and on the Pectic Fermentation.—G. Bertrand and A. Mallèvre.—The authors conclude that pectase exists in solution as well in the cellular juice of acid fruits as in that of the roots of carrots. There is no insoluble pectase.

MEETINGS FOR THE WEEK.

Tuesday, 25th.—Photographic, 8.
Wednesday, 26th.—Society of Arts, 4. (Anniversary).
— British Astronomical Association, 5.
Thursday, 27th.—Royal Society Club, 6.30. (Anniversary).
Friday, 28th.—Physical, 5. "An Electromagnetic Effect," by F. W. Bowden. "On Synchronous Motors," by W. G. Rhodes. "The Electrical Properties of Selenium," by Shelford Bidwell, F.R.S.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1857.

ON THE NEW SYSTEM OF CASTING CRUCIBLE STEEL INGOTS FOR TOOL MANUFACTURE.

By SERGIUS KERN, M.E., St. Petersburg.

In the Chemical News (vol. lxxi., pp. 187 and 220) some details were inserted concerning our proposed system of casting crucible steel ingots, used for forging various *tools*, not *bars*, for the market, as they would be in the majority of cases too short.

We cast now for trials, at the small steel-foundry of the New Admiralty, St. Petersburg, six flat ingots, which have a remarkably sound appearance (about 9"×9"; height, 3½ inches; weight, ⅔ cwt.).

On the surface is found a small cup-form piping, which is very shallow. In order to have the stream of steel, to go right into the middle of the mould, we used a burnt clay tumbler, ordinarily placed into the bottom of Siemens-Martin casting ladles, and 1⅛ inches diameter at the lower end. This tumbler is supported over the mould by the means of an iron ring with cross-bars.

The ready-melted steel is poured into an empty crucible heated to redness, containing 30 grms. of metallic aluminium, and from here into the first crucible again, and finally through the tumbler into the mould. The steel is covered with a lid 2" thick, and pulverised glass is thrown on its sides. The mould stands on a burnt clay smooth plate, and is slightly brushed inside with previously boiled gas-tar. The flat ingot produced is cleaned superficially by chiselling from the small cracks, &c.

In a short time I will send a report of the *modus operandi* of forging such ingots, the method of which was shortly mentioned in our notes in the above-named pages of the Chemical News. There is no nuisance at all if the cup-form piping happens to be somewhere near one of the corners of the square; the method of cutting the ingots under steam-hammer must only be slightly altered.

THE PRACTICAL WORKING OF PELOUZE'S PROCESS.

By VINCENT EDWARDS, F.C.S.

As manures sometimes contain nitrates of soda and potash, the latter salt especially being added when a concentrated mixture is required for garden purposes, the following notes may be useful to works chemists and others who wish to estimate rapidly the amount of nitric nitrogen, and have found this method as usually described troublesome and inaccurate:—

I use a 600 c.c. glass flask, with a good rubber stopper, fitted with a tube and a Bunsen valve, the opening in which is made with a razor, which is more satisfactory than a knife; as much depends upon the working of the valve, it is well to ascertain before commencing that it behaves correctly. The following solutions are required:—(1), 100 grms. crystallised sulphate of iron and 100 c.c. strong H_2SO_4, made up with water to 1 litre; (2), 14·742 grms. bichromate of potassium, made up to 1 litre with water; 1 c.c. of this = 0·0085 grm. $NaNO_3$, or 0·0101 grm. KNO_3. This strength, as recommended by Dr. Attfield, is very convenient.

If a nitrated manure is being examined, 10 grms. may be taken, treated with water, and filtered into a 200 c.c. flask, washed, and made up to the mark. The analysis is carried out thus:—50 c.c. of the iron solution with 20 c.c. (= 1 grm. manure) are run into the flask, the stopper inserted, and the flask placed on a sand-bath, the contents boiled till the liquid is so thick that semi-solid drops are splashed against the sides; the flask is then removed, a cloth put round it as there is danger of explosion, allowed to cool for some time; 100 c.c. of water then run in, and the titration with bichromate of potash solution carried out.

The following example will give an idea of the accuracy of this method under these conditions:—20 c.c. (= 1 grm. manure) treated as above, with 50 c.c. iron solution, 31 c.c. of bichromate required to oxidise the excess of ferrous iron. A blank titration showed that 50 c.c. iron = 54 c.c. bichromate; therefore 54 − 31 = 23 c.c. bichromate to complete oxidation, 23 × 0·0085 = 0·1955, or 19·55 per cent $NaNO_3$ in the manure. As the sample operated on was mixed carefully, thus—

20 parts 95·5 per cent $NaNO_3$
80 ,, ammoniacal guano
100

the calculated amount is 19·10 per cent $NaNO_3$, so the result, considering the well-known difficulty of this process is not unsatisfactory; the error, being less than 0·1 per cent of the nitrogen, if recorded as ammonia. In standardising the iron solution, I boil, say, 50 c.c., and on cooling titrate with bichromate, thus having about the same conditions in the trial and actual determination. The semi-solid matter in the flask is not very readily soluble; but this does not appear very necessary, as I am inclined to think the ferrous iron is immediately dissolved, which is all that is required. It is well to fix the end-point when a bright yellow colour is shown with a drop of ferricyanide on the slab.

Lawes' Works, Barking, Essex,
June 14, 1895.

POTASSIUM TETRAOXALATE AS A STANDARD IN ACIDIMETRY.

By ARTHUR BORNTRAEGER.

H. Borntraeger (*Chemiker Zeitung*, 1881, 519), as far as I know, was the first to propose the acid tartrate of potassium as a standard for alkali solutions. In 1892, I explained (*Zeit. f. Anal. Chemie*, 1892, 43) why I preferred it for that purpose to other substances, and also to the tetraoxalate of potassium. I gave then, and on other occasions (*Zeit. f. Anal. Chemie*, 1886, 327; *Zeit. f. Angewandte Chemie*, 1894, 54), special weight to the following facts:—

That the acid tartrate, which crystallises free from water, is easily obtained in a pure state; that it is scarcely hygroscopic; and that the dry salt may be preserved without alteration.

In mentioning the tetraoxalate amongst the substances that have been proposed by others, I objected (*Zeit. f. Anal. Chemie*, 1892, 43) that it contains water, and therefore might be liable to effloresce. It would be necessary, therefore, as I observed, either to make use of the dried salt or to determine each time the proportion of water. It is generally admitted that this salt loses its water when heated to 128° C. It further resulted from my paper that I did not consider it an easy thing to purify the tetraoxalate.

Wells (*Journ. Anal. and Appl. Chem.*, vi., 1892, 191) recognises the difficulties in preparing pure potassium tetraoxalate, and points out the tendency of this salt to effloresce. It was only through abstracts in a chemical journal (*Zeit. f. Anal. Chemie*, 1893, 452; 1894, 456) that I first became acquainted with the paper by Wells and a paper by B. C. Hinman (*Journ. Anal. and Appl. Chem.*, vi., 1892, 435). Of the latter I heard only recently. I have, however, read lately the original papers of both authors. Hinman, confirming, by his researches, those of W. Frear (*Vide* U.S. Department of Agriculture, Division of Chemistry, *Bulletin* No. 31, "Proceedings of the Eighth Annual Convention of the Association of Official Agricultural Chemists," August 13, 14, and 15, 1891, p. 131), concludes that potassium tetraoxalate is not adaptable as a standard for alkali solutions, since the preparation of that salt in a pure state offers great difficulties. He further points out that the salt in the dried state is hygroscopic, and that the salt containing water tends to effloresce.

As to Hinman's researches about the desiccation of the tetraoxalate at 128° C., I observe that I had not myself undertaken any experiments upon that question. That the salt gives off its water of crystallisation at that temperature is a fact I had simply taken from the best authorities (Gmelin, "Handbuch der Chemie," iv., 1848, 831; Wurtz, "Dictionnaire de Chimie, Pure et Appliquée," ii., 680; Watts, "Dictionary of Chemistry," 2nd ed., iv., 1883, 264). Gmelin (*loc. cit.*) attributes that assertion to Berzelius. I cannot, therefore, take upon myself any responsibility on that point, in which I simply relied on the exactitude of those who had studied the question.

Gabinetto di Tecnologia della R. Scuola
Superiore di Agricultura in Portici.

A REFORM IN CHEMICAL, PHYSICAL, AND TECHNICAL CALCULATIONS.

By C. J. HANSSEN, C.E.

(Continued from p. 164).

By similar calculation as used at p. 164 we find at normal atmospheric density and 0° N = 273° N absolute temperature, the weight and volume of compound gases. (See Table).

Heat.

If the specific heat of water at freezing-point is = 1, then the specific heat of hydrogen at constant pressure is = 3·400. For hydrogen, oxygen, carbon, nitrogen, and other simple gases, and for compounds which, in combining, have retained the original volume of the components, such as CO, is γ, or the ratio between specific heat at constant pressure and at constant volume exactly

$$\text{as } 17 : 12 = 1{\cdot}4166666 : 1.$$

The caloric work required to heat 1 kilogrm. H 1° N. consequently is:—

At constant pressure (heating and expanding) .. .. .. = 3·400 cal. = 17/5 calor.
At constant volume (heating without expanding) 3·400 cal. × 12/17 .. .. = 2·400 ,, = 12/5 ,,
The difference (expanding without heating) is 3·400 cal. × 5/17 .. .. = 1·000 ,, = 5/5 ,,

1 kilogrm. hydrogen is = 56/5 cbm.; consequently, to heat 1 cbm. H, of normal atmospheric density and 0° N., 1° N. requires—

At constant pressure.. .. $\frac{17\times 5}{5\times 56} = 17/56$ calor.
At constant volume .. .. $\frac{12\times 5}{5\times 56} = 12/56$,,
Expanding the volume .. $\frac{5\times 5}{5\times 56} = 5/56$,,

For other simple gases and for compounds which have retained their original volume, we find the heat required per kilogrm. by dividing the figures found per kilogrm. hydrogen by the relative weight of the gas in question.

Thus, per kilogrm. oxygen, is required—

At constant pressure.. .. $\frac{17}{5\times 16} = 17/80$ calor.
At constant volume .. .. $\frac{12}{5\times 16} = 12/80$,,
For expansion only .. .. $\frac{5}{5\times 16} = 5/80 = \frac{1}{16}$,,

To heat 1 cbm. of these gases (of normal density and temperature) 1° N. is required—exactly the same quantity of heat as for 1 cbm. of hydrogen.

Heating of *compound gases* which in combining have contracted in volume, requires per kilogrm.:—

At constant pressure $\frac{17}{5}$ cal. $\times \frac{\text{ratio of contraction}}{\text{relative weight}} = x$ cal.
At constant volume $\frac{12}{5}$ cal. $\times \frac{\text{ratio of contraction}}{\text{relative weight}} = x$,,
For expansion only $\frac{5}{5}$ cal. $\times \frac{\text{ratio of contraction}}{\text{relative weight}} = x$,,

and per cbm. of normal density and temperature is required the same quantity of heat as for hydrogen *multiplied* by the ratio of contraction of the gas in question.

Compound gases.		Ratio of contraction.	Relative weight.	1 cbm. weighs kilog. 1 litre = grm.	1 kilog. contains cbm. 1 grm. ,, litre.
Carbon monoxide,	CO	1 : 1	14	70/56 = 5/4	56/70 = 4/5 = 0·80000
Carbon dioxide,	CO_2	1½ : 1	22	110/56	56/110 = 0·50909
Methane,	CH_4	2½ : 1	8	40/56 = 5/7	56/40 = 7/5 = 1·40000
Acetylene,	C_2H_2	2 : 1	13	65/56	56/65 = 0·86154
Ethylene,	C_2H_4	3 : 1	14	70/56 = 5/4	56/70 = 4/5 = 0·80000
Ethane,	C_2H_6	4 : 1	15	75/56	56/75 = 0·74666
Allylene,	C_3H_4	3½ : 1	20	100/56 = 25/14	56/100 = 14/25 = 0·56000
Propylene,	C_3H_6	4½ : 1	21	105/56 = 15/8	56/105 = 8/15 = 0·53333
Propane,	C_3H_8	5½ : 1	22	110/56	56/110 = 28/55 = 0·50909
Elayl,	C_4H_8	3 : 1	14	70/56 = 5/4	56/70 = 4/5 = 0·80000
Butylene,	C_4H_8	6 : 1	28	140/56 = 5/2	56/140 = 2/5 = 0·40000
Butane,	C_4H_{10}	7 : 1	29	145/56	56/145 = 0·31500
Pentane,	C_5H_{12}	8½ : 1	36	180/56 = 45/14	56/180 = 14/45 = 0·31111
Benzene,	C_6H_6	6 : 1	39	195/56	56/195 = 0·28718
Dipropyl,	C_6H_{14}	10 : 1	43	215/56	56/215 = 0·26046
Sulphide of Hydr.,	SH_2	1½ : 1	17	85/56	56/85 = 0·65882
Ammonia,	NH_3	2 : 1	17/2	85/112	112/85 = 1·31765
Vapour of water,	H_2O	1½ : 1	9	45/56	56/45 = 1·24444

Thus, for *acetylene*—

	Per 1 kilogrm.		Per 1 cbm.	
At constant pressure	$\frac{17}{5} \times \frac{2}{13} = 34/65$	cal.	$\frac{17}{56} \times 2 = 17/28$	cal.
At constant volume	$\frac{12}{5} \times \frac{2}{13} = 24/65$	,,	$\frac{12}{56} \times 2 = 12/28$	,,
For expanding only	$\frac{5}{5} \times \frac{2}{13} = 10/65$	,,	$\frac{5}{56} \times 2 = 5/28$	,,

For *vapour of water*, H_2O,—

	Cal.	Cal.
At constant pressure ..	$\frac{17}{5} \times \frac{1\frac{1}{2}}{9} = 17/30$	$\frac{17}{56} \times 1\frac{1}{2} = 51/112$
At constant volume ..	$\frac{12}{5} \times \frac{1\frac{1}{2}}{9} = 12/30 = \frac{2}{5} = 0{\cdot}4$	$\frac{12}{56} \times 1\frac{1}{2} = 36/112$
For expanding only	$\frac{5}{5} \times \frac{1\frac{1}{2}}{9} = 5/30 = \frac{1}{6}$	$\frac{5}{56} \times 1\frac{1}{2} = 15/112$

Ice and *liquid water* hermetically inclosed are H_2O at constant volume.

Errata.—In the Table at foot of page 163, 3rd line, "10·7" should read "10/7"; 4th line, "4/5" should read "5/4."

(To be continued).

3, Valdemarsgade, Copenhagen, V.
May 6, 1895.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending May 31st, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 14th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 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 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 whole of the 189 samples examined were found to be clear, bright, and efficiently filtered.

The month of May has been remarkably dry, the total rainfall at Oxford, representing the Thames valley, being only 0·16 inch. As the 25 years' mean for the month is 1·95 inch, the deficiency is no less than 1·79 inch. What little rain there was fell on four days, the 1st, 17th, 23rd, and 30th.

It has usually been found that the river water in dry summer months is of a somewhat higher degree of purity than when the summer is wet. On comparing the chemical composition of the waters during May with their composition in April when the mean amount of rain fell, it will be seen that the improvement, although perceptible, is not so striking as it formerly was when the present high degree of purity was not so uniformly reached. It therefore appears that the filtering plant of the several Companies is quite sufficient to preserve the high standard of purity, irrespective of occasional influxes into the river of vegetable and peaty organic matter due to sudden or long-continued rain. The chief improvement is in the organic carbon and the colour.

On the other hand, bacteriological examinations show the improvement due to the dry season in a marked manner. The filtered water from the general wells at the works during the month of May contained an average of 18 microbes per cubic centimetre, as against 46 in the month of April, whilst the unfiltered water contained 4070 per cubic centimetre.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

THE OXYHYDROGEN ACCUMULATOR.

By H. N. WARREN, Research Analyst.

Grove's oxyhydrogen battery, better known as the gas battery, in its simplest form consists of two strips of platinum foil, each strip being exposed, one to the action of hydrogen gas, the other to that of oxygen, contained in suitable receptacles.

Based upon a somewhat similar theory, while at the same time taking advantage of the peculiar surface action that the element palladium exerts when exposed to an atmosphere of hydrogen, the author has constructed batteries according to the following method:—He takes an ordinary Woulff's bottle containing acidulated water, into which are inserted two tubes, constructed by fusing into the glass tubes two platinum wires, terminating in a platinum plate for the oxygen tube, and one of palladium for the hydrogen tube, each tube being filled with its respective gas. Several cells thus arranged in series have been found to produce a mean voltage of 0·45, while by rendering the surface more active even 0·5 has been attained, a series of five such batteries being capable of decomposing water. The next experiments performed were with a view of increasing the pressure of each gas, and here the first danger presents itself,

Subjected to 180 atmospheres pressure, the mixed gases had been found on previous occasions to unite with great violence, whereas by increased surface action they combine at even diminished pressure. At the same time, the consumption of hydrogen being double that of the oxygen in its union to form water, a further difficulty presents itself as regards regulating the pressure; and in order to produce a greater surface action plates of graphite were prepared, some platinised and others palladinised, each being exposed to the action of its respective gas by enclosing the same in steel canisters lined with lead, and furnished with a water-gauge in order to indicate the level and ensure the existence of an even pressure.

Both gases were now introduced under two atmospheres pressure, and were somewhat quickly absorbed, an increase of every two atmospheres increasing the voltage by about 0·15 volt, until 1 volt was reached, and in one case even 1·25 was attained.

Experiments are now being carried out with respect to maintaining a more steady pressure, and to rendering the apparatus less dangerous as regards an explosive mixture being formed; when this is accomplished, together with the removal of other small difficulties which still exist, it will probably be possible to construct a self-charging accumulator.

Liverpool Research Laboratory,
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ARGON.*

By the Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D., F.R.S., Professor of Natural Philosophy, R.I.

(Concluded from p. 302).

I HAVE said enough about this method, and I must now pass on to the alternative method which has been very successful in Professor Ramsay's hands—that of absorbing nitrogen by means of red-hot magnesium. By the kindness of Professor Ramsay and Mr. Matthews, his assistant, we have here the full scale apparatus before us almost exactly as they use it. On the left there is a reservoir of nitrogen derived from air by the simple removal of oxygen. The gas is then dried. Here it is bubbled through sulphuric acid. It then passes through a long tube made of hard glass and charged with magnesium in the form of thin turnings. During the passage of the gas over the magnesium at a bright red heat, the nitrogen is absorbed in a great degree, and the gas which finally passes through is immensely richer in argon than that which first enters the hot tube. At the present time you see a tolerably rapid bubbling on the left, indicative of the flow of atmospheric nitrogen into the combustion furnace; whereas, on the right, the outflow is very much slower. Care must be taken to prevent the heat rising to such a point as to soften the glass. The concentrated argon is collected in a second gasholder, and afterwards submitted to further treatment. The apparatus employed by Professor Ramsay in the subsequent treatment is exhibited in the diagram, and is very effective for its purpose; but I am afraid that the details of it would not readily be followed from any explanation that I could give in the time at my disposal. The principle consists in the circulation of the mixture of nitrogen and argon over hot magnesium, the gas being made to pass round and round until the nitrogen is effectively removed from it. At the end that operation, as in the case of the oxygen method, proceeds somewhat slowly. When the greater part of the nitrogen is gone, the remainder seems to be unwilling to follow, and it requires somewhat protracted treatment in order to be sure that the nitrogen has wholly disappeared. When I say "wholly disappeared," that perhaps would be too much to say in any case. What we can say is, that the spectrum test is adequate to show the presence, or at any rate to show the addition, of about one-and-a-half per cent of nitrogen to argon as pure as we can get it; so that it is fair to argue that any nitrogen at that stage remaining in the argon is only a small fraction of one-and-a-half per cent.

I should have liked at this point to be able to give advice as to which of the two methods—the oxygen method or the magnesium method—is the easier and the more to be recommended; but I confess that I am quite at a loss to do so. One difficulty in the comparison arises from the fact that they have been in different hands. As far as I can estimate, the quantities of nitrogen eaten up in a given time are not very different. In that respect, perhaps, the magnesium method has some advantage; but, on the other hand, it may be said that the magnesium process requires a much closer supervision, so that, perhaps, fourteen hours of the oxygen method may not unfairly compare with eight hours or so of the magnesium method. In practice a great deal would depend upon whether in any particular laboratory alternate currents are available from a public supply. If the alternate currents are at hand, I think it may probably be the case that the oxygen method is the easier; but, otherwise, the magnesium method would probably be preferred, especially by chemists who are familiar with operations conducted in red-hot tubes.

I have here another experiment illustrative of the reaction between magnesium and nitrogen. Two rods of that metal are suitably mounted in an atmosphere of nitrogen, so arranged that we can bring them into contact and cause an electric arc to form between them. Under the action of the heat of the electric arc the nitrogen will combine with the magnesium; and if we had time to carry out the experiment we could demonstrate a rapid absorption of nitrogen by this method. When the experiment was first tried, I had hoped that it might be possible, by the aid of electricity, to start the action so effectively that the magnesium would continue to burn independently under its own developed heat in the atmosphere of nitrogen. Possibly, on a larger scale, something of this sort might succeed, but I bring it forward here only as an illustration. We turn on the electric current, and bring the magnesiums together. You see a brilliant green light, indicating the vaporisation of the magnesium. Under the influence of the heat the magnesium burns, and there is collected in the glass vessel a certain amount of brownish-looking powder which consists mainly of the nitride of magnesium. Of course, if there is any oxygen present it has the preference, and the ordinary white oxide of magnesium is formed.

The gas thus isolated is proved to be inert by the very fact of its isolation. It refuses to combine under circumstances in which nitrogen, itself always considered very inert, does combine, both in the case of the oxygen treatment and in the case of the magnesium treatment; and these facts are, perhaps, almost enough to justify the name which we have suggested for it. But, in addition to this, it has been proved to be inert under a considerable variety of other conditions such as might have been expected to tempt it into combination. I will not recapitulate all the experiments which have been tried, almost entirely by Professor Ramsay, to induce the gas to combine. Hitherto, in our hands, it has not done so; and I may mention that recently, since the publication of the abstract of our paper read before the Royal Society, argon has been submitted to the action of titanium at a red heat, titanium being a metal having a great affinity for nitrogen, and that argon has resisted the temptation to which nitrogen succumbs. We never have asserted, and we do not now assert, that argon can under no circumstances be got to combine. That would, indeed, be a rash assertion for any one to venture upon; and only within the last few weeks there has been a most interesting announcement by M. Berthelot, of Paris, that, under the action of the silent electric discharge, argon can be absorbed when treated in contact with the vapour of benzine. Such a statement, coming from so great an authority, commands our attention; and if we accept the conclusion, as I suppose we must do, it will follow that argon has, under those circumstaces, combined.

Argon is rather freely soluble in water. That is a thing that troubled us at first in trying to isolate the gas; because, when one was dealing with very small quantities, it seemed to be always disappearing. In trying to accumulate it we made no progress. After a sufficient quantity had been prepared, special experiments were made on the solubility of argon in water. It has been found that argon, prepared both by the magnesium method and by the oxygen method, has about the same solubility in water as oxygen—some two-and-a-half times the solubility of nitrogen. This suggests, what has been verified by experiment, that the dissolved gases of water should contain a larger proportion of argon than does atmospheric nitrogen. I have here an apparatus of a somewhat rough description, which I have employed in experiments of this kind. The boiler employed consists of an old oil-can. The water is supplied to it and drawn from it by coaxial tubes of metal. The incoming cold water flows through the outer annulus between the two tubes. The outgoing hot water passes through the inner tube, which ends in the interior of the vessel at a higher level. By means of this arrangement the heat of the water which has done its work is passed on to the incoming water not yet in operation, and in that way a limited amount of heat is made

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* A Lecture delivered at the Royal Institution of Great Britain Friday, April 5, 1895.

to bring up to the boil a very much larger quantity of water than would otherwise be possible, the greater part of the dissolved gases being liberated at the same time. These are collected in the ordinary way. What you see in this flask is dissolved air collected out of water in the course of the last three or four hours. Such gas, when treated as if it were atmospheric nitrogen, that is to say after the removal of the oxygen and minor impurities, is found to be decidedly heavier than atmospheric nitrogen to such an extent as to indicate that the proportion of argon contained is about double. It is obvious, therefore, that the dissolved gases of water form a convenient source of argon, by which some of the labour of separation from air is obviated. During the last few weeks I have been supplied from Manchester by Mr. Macdougall, who has interested himself in this matter, with a quantity of dissolved gases obtained from the condensing water of his steam-engine.

As to the spectrum, we have been indebted from the first to Mr. Crookes, and he has been good enough to-night to bring some tubes which he will operate, and which will show you at all events the light of the electric discharge in argon. I cannot show you the spectrum of argon, for unfortunately the amount of light from a vacuum tube is not sufficient for the projection of its spectrum. Under some circumstances the light is red, and under other circumstances it is blue. Of course when these lights are examined with the spectroscope—and they have been examined by Mr. Crookes with great care—the differences in the colour of the light translate themselves into different groups of spectrum lines. We have before us Mr. Crookes's map, showing the two spectra upon a very large scale. The upper is the spectrum of the blue light; the lower is the spectrum of the red light; and it will be seen that they differ very greatly. Some lines are common to both; but a great many lines are seen only in the red, and others are seen only in the blue. It is astonishing to notice what trifling changes in the conditions of the discharge bring about such extensive alterations in the spectrum.

One question of great importance, upon which the spectrum throws light is, Is the argon derived by the oxygen method really the same as the argon derived by the magnesium method? By Mr. Crookes's kindness I have had an opportunity of examining the spectra of the two gases side by side, and such examination as I could make revealed no difference whatever in the two spectra, from which, I suppose, we may conclude either that the gases are absolutely the same, or, if they are not the same, that at any rate the ingredients by which they differ cannot be present in more than a small proportion in either of them.

My own observations upon the spectrum have been made principally at atmospheric pressure. In the ordinary process of sparking, the pressure is atmospheric; and, if we wish to look at the spectrum, we have nothing more to do than to include a jar in the circuit, and to put a direct-vision prism to the eye. At my request, Professor Schuster examined some tubes containing argon at atmospheric pressure prepared by the oxygen method, and I have here a diagram of a characteristic group. He also placed upon the sketch some of the lines of zinc, which were very convenient, as directing one exactly where to look. (See Fig.).

Within the last few days, Mr. Crookes has charged a radiometer with argon. When held in the light from the electric lamp, the vanes revolve rapidly. Argon is anomalous in many respects, but not, you see, in this.

Next, as to the density of argon. Professor Ramsay has made numerous and careful observations upon the density of the gas prepared by the magnesium method, and he finds a density of about 19·9 as compared with hydrogen. Equally satisfactory observations upon the gas derived by the oxygen method have not yet been made, but there is no reason to suppose that the density is different, such numbers as 19·7 having been obtained.

One of the most interesting matters in connection with argon, however, is what is known as the ratio of the specific heats. I must not stay to elaborate the questions involved, but it will be known to many who hear me that the velocity of sound in a gas depends upon the ratio of two specific heats—the specific heat of the gas measured at constant pressure, and the specific heat measured at constant volume. If we know the density of a gas, and also the velocity of sound in it, we are in a position to infer this ratio of specific heats; and by means of this method, Professor Ramsay has determined the ratio in the case of argon, arriving at the very remarkable result that the ratio of specific heats is represented by the number 1·65, approaching very closely to the theoretical limit, 1·67. The number 1·67 would indicate that the gas has no energy except energy of translation of its molecules. If there is any other energy than that, it would show itself by this number dropping below 1·67. Ordinary gases, oxygen, nitrogen, hydrogen, &c., do drop below, giving the number 1·4. Other gases drop lower still. If the ratio of specific heats is 1·65, practically 1·67, we may infer then that the whole energy of motion is translational; and from that it would seem to follow by arguments which, however, I must not stop to elaborate, that the gas must be of the kind called by chemists monatomic.

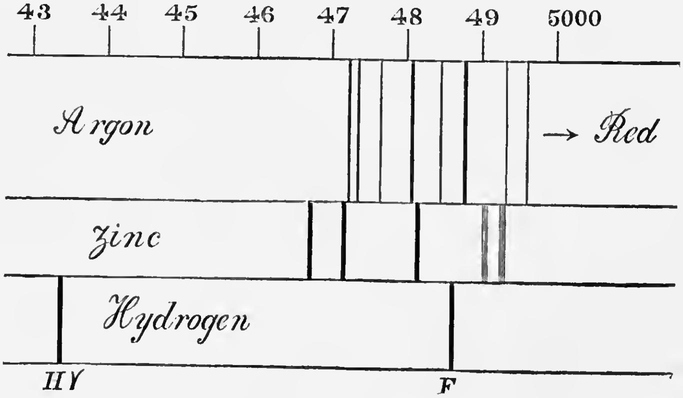
I had intended to say something of the operation of determining the ratio of the specific heats, but time will not allow. The result is, no doubt, very awkward. Indeed, I have seen some indications that the anomalous properties of argon are brought as a kind of accusation against us. But we had the very best intentions in the matter. The facts were too much for us; and all we can do now is to apologise for ourselves and for the gas.

Several qnestions may be asked, upon which I should like to say a word or two, if you will allow me to detain you a little longer. The first question (I do not know whether I need ask it) is, Have we got hold of a new gas at all? I had thought that that might be passed over, but only this morning I read in a technical journal the suggestion that argon was our old friend nitrous oxide. Nitrous oxide has roughly the density of argon; but that, as far as I can see, is the only point of resemblance between them.

Well, supposing that there is a new gas, which I will not stop to discuss, because I think the spectrum alone would be enough to prove it, the next question that may be asked is, Is it in the atmosphere? This matter naturally engaged our earnest attention at an early stage of the enquiry. I will only indicate in a few words the arguments which seem to us to show that the answer must be in the affirmative.

In the first place, if argon be not in the atmosphere, the original discrepancy of densities which formed the starting point of the investigation remains unexplained, and the discovery of the new gas has been made upon a false clue. Passing over that, we have the evidence of the blank experiments, in which nitrogen originally derived from chemical sources is treated either with oxygen or with magnesium, exactly as atmospheric nitrogen is treated. If we use atmospheric nitrogen, we get a certain proportion of argon, about 1 per cent. If we treat chemical nitrogen in the same way we get, I will not say absolutely nothing, but a mere fraction of what we should get had atmospheric nitrogen been the subject. You may ask, Why do we get any fraction at all from chemical nitrogen? It is not difficult to explain the small residue, because in the manipulation of the gases large quantities of water are used; and, as I have already explained, water dissolves argon somewhat freely. In the processes of manipulation some of the argon will come out of solution, and it remains after all the nitrogen has been consumed.

Another wholly distinct argument is founded upon the method of diffusion introduced by Graham. Graham showed that if you pass gas along porous tubes you alter the composition, if the gas is a mixture. The lighter constituents go more readily through the pores than do the heavier ones. The experiment takes this form :—A number of tobacco-pipes—eight in the actual arrangement—are joined together in series with indiarubber junctions, and they are put in a space in which a vacuum can be made, so that the space outside the porous space is vacuous or approximately so. Through the pipes ordinary air is led. One end may be regarded as open to the atmosphere. The other end is connected with an aspirator so arranged that the gas collected is only some two per cent of that which leaks through the porosities. The case is like that of an Australian river drying up almost to nothing in the course of its flow. Well, if we treat air in that way, collecting only the small residue which is less willing than the remainder to penetrate the porous walls, and then prepare "nitrogen" from it by removal of oxygen and moisture, we obtain a gas heavier than atmospheric nitrogen, a result which proves that the ordinary nitrogen of the atmosphere is not a simple body, but is capable of being divided into parts by so simple an agent as the tobacco-pipe.



If it be admitted that the gas is in the atmosphere, the further question arises as to its nature.

At this point I would wish to say a word of explanation. Neither in our original announcement at Oxford, nor at any time since, until the 31st of January, did we utter a word suggesting that argon was an element; and it was only after the experiments upon the specific heats that we thought that we had sufficient to go upon in order to make any such suggestion in public. I will not insist that that observation is absolutely conclusive. It is certainly strong evidence. But the subject is difficult, and one that has given rise to some difference of opinion among physicists. At any rate this property distinguishes argon very sharply from all the ordinary gases.

One question which occurred to us at the earlier stage of the enquiry, as soon as we knew that the density was not very different from 21, was the question of whether, possibly, argon could be a more condensed form of nitrogen, denoted chemically by the symbol N_3. There seem to be several difficulties in the way of this supposition. Would such a constitution be consistent with the ratio of specific heats (1·65)? That seems extremely doubtful. Another question is, Can the density be really as high as 21, the number required on the supposition of N_3? As to this matter, Professor Ramsay has repeated his measurements of density, and he finds that he cannot get even so high as 20. To suppose that the density of argon is really 21, and that it appears to be 20 in consequence of nitrogen still mixed with it, would be to suppose a contamination with nitrogen out of all proportion to what is probable. It would mean some 14 per cent of nitrogen, whereas it seems that from one-and-a-half to two per cent is easily enough detected by the spectroscope. Another question that may be asked is, Would N_3 require so much cooling to condense it as argon requires?

There is one other matter on which I would like to say a word—the question as to what N_3 would be like if we had it. There seems to be a great discrepancy of opinions. Some high authorities, among whom must be included, I see, the celebrated Mendeleeff, consider that N_3 would be an exceptionally stable body; but most of the chemists with whom I have consulted are of opinion that N_3 would be explosive, or, at any rate, absolutely unstable. That is a question which may be left for the future to decide. We must not attempt to put these matters too positively. The balance of evidence still seems to be against the supposition that argon is N_3, but for my part I do not wish to dogmatise.

A few weeks ago we had an eloquent lecture from Prof. Rücker on the life and work of the illustrious Helmholtz. It will be known to many that during the last few months of his life Helmholtz lay prostrate in a semi-paralysed condition, forgetful of many things, but still retaining a keen interest in science. Some little while after his death we had a letter from his widow, in which she described how interested he had been in our preliminary announcement at Oxford upon this subject, and how he desired the account of it to be read to him over again. He added the remark, "I always thought that there must be something more in the atmosphere."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 6th, 1895.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Messrs. G. E. Shaw, H. Thornton, and H. F. A. Wigley were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George Percy Bailey, B.A., 7, Mount Pleasant Square, Dublin; Charles James Fawel, The Laboratory, Cranford, Middlesex; Jervis E. Foakes, Medical School, Caxton Street, Westminster, S.W.; Stanley Fox, 46, Preston Street, Faversham: Rev. Henry Arthur Hall, M.A., The Schoolhouse, Totnes; James Henderson, B.Sc., 193, Blackness Road, Dundee; William Henry Pennington, Firedhouse, Rochdale; W. T. B. Ridge, 2, Ashwood Terrace, Longton, Staffs.; William Augustus Rugginz, 114, Upton Lane, Forest Gate, E.; W. T. Tibbald, 72, Lafayette Avenue, Detroit, U.S.A.; Harold E. Wright, Springhurst, Hartburn, Stockton-on-Tees.

It was announced from the Chair that on Thursday, June 20th, an Extraordinary General Meeting of the Society would be held at 8 p.m., to vote on the following change in the Bye-law which is proposed by the Council:—

- In Bye-law 1 to strike out the last paragraph, beginning "The life composition fee," and insert the following:—"The life composition fee shall be £30, excepting that Fellows who have paid ten annual subscriptions shall pay as life composition fee £20; Fellows who have paid fifteen annual subscriptions shall pay £15; Fellows who have paid twenty annual subscriptions shall pay £12; and Fellows who have paid twenty-five annual subscriptions shall pay £10."

Of the following papers those marked * were read :—

*74. *The Molecular Refractions of Dissolved Salts and Acids.*" By Dr. J. H. Gladstone, F.R.S., and Walter Hibbert.

In a paper on the "Refraction Equivalents of the Elements" (*Phil. Trans.*, 1870), Dr. Gladstone gave reasons for believing that the molecular refraction of a salt or acid is not altered when dissolved in water. Some controversy arose upon this point, and the refraction of salts in solution has been the subject of investigation by many experimenters. The present communication is devoted to a rigid examination of two of the reasons previously assigned:—

1st. The similarity of the molecular refraction of substances when determined from the solid and from its solution.

2nd. That the molecular refraction of a dissolved salt is not affected by varying the amount of water.

The data employed in the present investigation are:— Dr. Gladstone's former observations of 1869 and 1891, wherever sufficiently reliable; the published observations of other experimenters; and numerous series of observations recently made by Mr. Hibbert.

The results are arranged in tables. One of these exhibits the refraction values of all the solid salts which have been determined, provided they have but one index of refraction, together with a few others. These are compared with the refraction of the same salt in a nearly saturated solution. Another gives the same for anhydrous acids and their strong solutions. A third shows the effect upon refraction of diluting a strong solution of the salt or acid.

The combined results of these investigations are made apparent to the eye in five diagrams containing respectively the principal observations on the chlorides, the other haloid salts, the nitrates, the sulphates, and the acids themselves. These diagrams represent the specific refractive energy of the substance before solution, and then upon the addition of varying proportions of water. By far the greatest change occurs with hydrochloric acid, which rises from 0·30 to nearly 0·39 when dissolved in 1·5 times its weight of water, and to 0·40 in very dilute solutions. Many other salts and acids show a distinct, but much smaller, increase, while in others, again, if there be any change, it is within the limits of errors of observation. Various points of relationship between these variations and the chemical nature of the binary compounds examined are pointed out.

This investigation explains some of the difficulties met with in the original determinations of refraction equivalents, and will be of great service in any future revision of them.

The general conclusion is that when a salt or acid dissolves in water the law of permanency of specific refractive energy, notwithstanding change of physical condition, does hold good; but that in many, if not most, cases there is some circumstance which causes a slight departure from it, while with the "strong acids" the departure is considerable. This change takes place principally in the initial stage of solution of the solid or liquid compound; but in many cases a small further change is discernible as more and more water is added; but this soon becomes inappreciable. This change is, in some cases, in the direction of an increased refraction, especially in the haloid salts and the acids; in other cases, especially the nitrates and salts of low refractive energy, this change is in the opposite direction. In either case the dilution effect is in the same direction as that due to solution. In a few cases, where the dispersion was capable of being estimated, the change in it was found to be proportionally greater than the change in the refraction itself. The origin of this refraction change is at present obscure, but it probably arises from some gradual change in the arrangement of the atoms or molecules of the salt or acid under the influence of water; and there are clear indications of some connection between the amount of this change and the amount of the specific refractive energy of the salts themselves. It stands also in some relation to the phenomena of electric conductivity, and especially of magnetic rotation.

*75. "*A Comparison of some Properties of Acetic Acid, and its Chloro- and Bromo-derivatives.* By S. U. Pickering, F.R.S.

The properties which have been examined are, in the cases of acetic acid and its chloro-derivatives, the heat of fusion, heat capacities both as solids and liquids, heat of dissolution, heat of dilution, and freezing-points when mixed with water; the boiling-points, densities, and magnetic rotations are also compared with these. In the case of the bromo-derivatives, the heat of dissolution of the solids alone was determined.

As regards the boiling-point, heat capacity of liquid, density, and heat of dissolution, acetic acid appears to occupy an exceptional position when compared with its chloro-derivatives, whereas, as regards the freezing-point, magnetic rotation, and heat of dilution, the alternate members of the series show a close relationship with each other.

Monochloracetic acid was found to exist in four distinct crystalline modifications, differing from each other in their melting-points by about 5°. Any of these modifications can be obtained at will, either from the liquid acid or from mixtures of it with water. The most stable form (the α) possesses a heat of fusion, and, hence, a heat of dissolution, when solid, about 500 cal. greater (negatively) than that of the β-modification; and from the fact that the heat absorbed on dissolution appears to be exceptionally large when compared with that absorbed by the other chlorinated acids, it is probable that these are in a form comparable with one of the less stable modifications of chloracetic acid. A similar exceptional position is occupied by monobromacetic acid amongst its congeners, but all attempts to obtain other modifications of this acid failed.

76. "*ββ-Dinaphthyl and its Quinones.*" By F. D Chattaway, B.A.

Although several substances of the compositon $C_{20}H_{14}$, differing considerably in melting-point and physical properties, have been prepared, the constitution of only one of these, $\alpha\alpha$-dinaphthyl, is known.

The present paper contains an account of the synthesis of $\beta\beta$-dinaphthyl, of its qninones, and of some closely-related derivatives.

$\beta\beta$-Dinaphthyl is obtained by the action of sodium on β-chloronapththalene dissolved in boiling xylene in presence of a small quantity of ethyl acetate. It is also produced when zinc-dust acts on β-diazonaphthalene sulphate dissolved in alcohol. It crystallises well and completely from benzene or xylene, in large, colourless plates, having a slight blue fluorescence. It is easily soluble in boiling benzene, xylene, and glacial acetic acid, much less soluble in alcohol. It sublimes readily, but is not volatile with steam. It melts at 183·5°, and boils at 452° under a pressure of 753 m.m. Its molecular weight, determined by the depression of the freezing-point of a benzene solution, agrees very closely with the calculated number.

When dissolved in glacial acetic acid and oxidised by chromic acid, one or other of two quinones can be obtained, according to the conditions under which the oxidation is performed. If the oxidation be effected rapidly in boiling glacial acetic acid, a quinone is produced in almost theoretical quantities, whose composition and molecular weight agree with the formula $C_{20}H_{12}O_2$. This is an orange-yellow substance, melting at 177°, and crystallising in very small needles, generally aggregated into rosettes. It is easily soluble in alcohol, ethyl acetate, glacial acetic acid, and benzene. It yields a colourless hydroquinone on reduction, and dissolves easily in cold concentrated sulphuric acid with a very characteristic indigo-blue colour. Its appearance and behaviour lead to the conclusion that it is a paraquinone analogous to α-naphthoquinone (1 . 4) having the constitution—

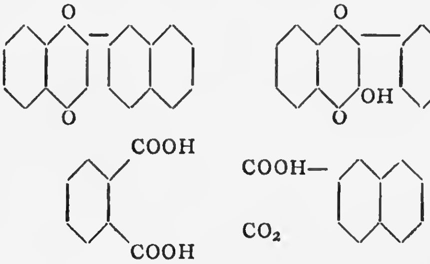
$$C_{10}H_5O{\cdot}C_{10}H_7{\cdot}O \ (1\ .\ 2\ .\ 4).$$

When this quinone is heated with a solution of potassium hydroxide, one of its hydrogen atoms is displaced, the hydrogen liberated reducing the quinone—

$$C_{20}H_{12}O_2 + KOH = C_{20}H_{11}(OH)_2OK.$$

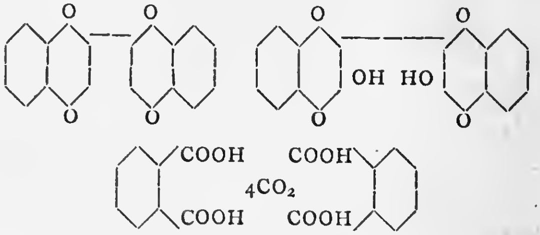
If this action takes place in presence of air, the two hydroxyl groups are at once oxidised, the potassium derivative, $C_{20}H_{11}O_2(OK)$, of a hydroxyquinone being formed, from which a hydroxyquinone is set free on addition of an acid. It is a light red, crystalline powder, which melts at about 186—187°, readily soluble in alcohol, benzene, glacial acetic acid, and ethyl acetate, and its composition and molecular weight show that it is derived from the quinone by the replacement of a hydrogen atom by a hydroxyl group. This compound, when dissolved in a hot solution of potassium hydroxide and oxidised by a solution of potassium permanganate, yields phthalic acid, carbon dioxide, and β-naphthoic acid.

This seems to show that the quinone is really β-naphthyl naphthoquinone, $C_{10}H_5{\cdot}O{\cdot}C_{10}H_7{\cdot}O$ (1 . 2 . 4), the replacement of hydrogen by hydroxyl and the breaking down of the molecule taking place as follows.



The second quinone, $C_{20}H_{10}O_4$, is produced in small quantity if a considerable excess of chromic acid is used in the oxidation and if the action is prolonged. It can easily be separated from β-naphthyl-naphthoquinone by its slight solubility in alcohol. It is probably formed by the further oxidation of the naphthyl naphthoquinone, as it is always accompanied by more or less of that substance and by tarry decomposition products.

The quinone, $C_{20}H_{10}O_4$, is a light brown, somewhat earthy-looking powder, the particles having no definite crystalline shape. It is moderately soluble in boiling glacial acetic acid and benzene, slightly in hot alcohol. It melts at about 216—217°, and gives a deep orange colour with cold concentrated sulphuric acid. It behaves very much like the simpler quinone, its behaviour being modified apparently by its containing two naphthoquinone groups instead of one. When heated with a solution of potassium hydroxide, it is dissolved, forming a dipotassium derivative, the liberated hydrogen, as before, reducing the quinone, $C_{20}H_{10}O_4 + 2KOH = C_{20}H_8(OH)_4(OK)_2$. In presence of air, the hydroxyl groups are oxidised, and, on addition of an acid, a dihydroxydiquinone of the composition $C_{20}H_8O_4(OH)_2$, is thrown down. This forms a dark red, almost black, powder, which gives a red streak on unglazed porcelain. It melts near 215°, and is easily soluble in glacial acetic acid, ethyl acetate, and alcohol. When dissolved in a boiling solution of potassium hydroxide and oxidised by a solution of potassium permanganate, it yields apparently only phthalic acid and carbon dioxide, which makes it probable that the quinone is ββ-di-α-naphthoquinone, $C_{10}H_5O_2{\cdot}C_{10}H_5O_2$ (1 . 2 . 4 . 1 . 2 . 4), the actions being represented as follows.

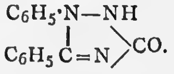


77. "*Action of Benzaldehyde on Phenylsemicarbazide.*" By George Young, Ph.D.

When alcoholic solutions of benzaldehyde and phenylsemicarbazide are evaporated to dryness, reaction occurs according to the equation—

$$C_7H_9N_3O + C_7H_6O + O = C_{14}H_{11}N_3O + 2H_2O.$$

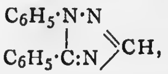
The yield is much increased by adding an oxidising agent such as ferric chloride. The product, which has slight basic and decided acid properties, is a diphenyloxytriazol,



$$\begin{array}{l} C_6H_5{\cdot}N\text{—}NH \\ \quad\ \ | \qquad\ \ \rangle CO. \\ C_6H_5\,C{=}N \end{array}$$

The silver salt, $C_{14}H_{10}N_3OAg + H_2O$, and the hydrochloride, $C_{14}H_{11}N_3OHCl + 2H_2O$, have been prepared; the latter is dissociated by water. The acetyl derivative, $C_{14}H_{10}N_3O(C_2H_3O)$ (m. p. 133°) is prepared by the action of acetic anhydride and sodium acetate. The ethylic ether, $C_{14}H_{10}N_3O(C_2H_5)$ (m. p. 92°) is prepared by the action of ethyl iodide on the silver salt or by heating diphenyloxytriazol with potassium hydroxide, ethyl iodide, and ethyl alcohol for an hour in a sealed tube at 100°.

The diphenyloxytriazol is reduced to diphenyltriazol, a weak base—



$$\begin{array}{l} C_6H_5{\cdot}N{\cdot}N \\ \quad\ \ | \qquad \rangle CH, \\ C_6H_5{\cdot}C{:}N \end{array}$$

(m. p. 91°), by heating with phosphorus pentasulphide to 230—250°, for six hours; its hydrochloride—

$$C_{14}H_{11}N_3HCl + 2H_2O,$$

and its platinichloride, $(C_{14}H_{11}N_3HCl)_2PtCl_4 + 4H_2O$, are both dissociated by water. The latter on being heated to 180° loses besides its water of crystallisation 4 molecular proportions of hydrochloric acid.

78. "*Note on the Latent Heat of Fusion.*" By N. F. Deerr.

If, in Mr. Crompton's relation (*Trans.*, cxlv., 240), $Aw/Tv = C$, 1/S where S is the specific heat, be substituted for A, we obtain $w/STv = C$, and when the valency is constant, $w/ST = C$.

In order that this relation may have a definite meaning, w/S must be temperature, or, symbolically, $w/S = T'$.

Then $w = ST'$, which, since w is quantity of heat, as is also ST', is a true relation. For the quantity w/S I would propose the term "temperature equivalent of latent heat of fusion," so that Mr. Crompton's relation may be expressed :—"When the valency of any series of elements is the same, the temperature equivalent of the latent heat of fusion bears a constant ratio to the absolute temperature of the melting point.

Denoting the temperature equivalent of the latent heat of fusion by T*f*, and temperature of the melting point by T, the table below includes values of T/T*f* for all the elements for which w is known; it will appear that there are exceptions to the rule, but that in the majority of cases the agreement is most striking.

Monads.

Elements.	T*f*.	T.	T/T*f*.
Sodium	111	365	3·32
Potassium	94	335	3·57
Silver	377	1220	3·25
Thallium..	167	565	3·35
Bromine	151	266	1·76
Iodine	217	386	1·78

Between the metallic elements considered separately, and also between the non-metallic elements, there is a remarkable agreement; it would not, however, be expected that there would be a law connecting elements with such widely varying properties as, say, bromine and sodium; it is, however, worthy of notice that the value of T/T*f* for bromine and iodine is very nearly half that for the metallic monad elements.

Dyads.

Elements.	T*f*.	T.	T/T*f*.
Zinc..	299	695	2·32
Cadmium	252	601	2·38
Mercury	90·5	233	2·58
Palladium	625	1700	2·72
Platinum..	875	2050	2·34
Lead	174	603	3·47
Tin	253	503	1·99

Lead and tin are taken as dyads: with the exception of the disagreement shown by these elements, the values of T/T*f* are quite satisfactory.

Triads.

Elements.	T*f*.	T.	T/T*f*.
Gallium	238	286	1·20
Phosphorus	25	317	12·05
Bismuth	434	535	1·23
Gold..	510	1328	2·60

The agreement between gallium and bismuth is satisfactory, and gold, although evidently triad, is better included with platinum and palladium; of the abnormal value of phosphorus I can give no explanation; it will be remembered, however, that in Mr. Crompton's relation the reciprocal of the valency was taken.

Tetrads.

Elements.	T*f*.	T.	T/T*f*.
Sulphur	57·5	385	6·70
Aluminium	133	870	6·55

Sulphur is taken as a tetrad, as it appears in the dioxide; the close agreement between sulphur and aluminium, perhaps, justifying this.

79. "*Acid Compounds of some Natural Yellow Colouring Matters.*" (Part I.). By A. G. PERKIN and L. PATE.

In a previous communication by one of us (*Ber.*, xv., 2337) an account was given of some peculiar acid compounds formed by the action of mineral acids upon hæmatein and brazilein, the colouring matters of logwood and brazil-wood. In continuation of this work the behaviour of acids towards various natural yellow colouring matters has been studied, the results of which are embodied in the accompanying table.

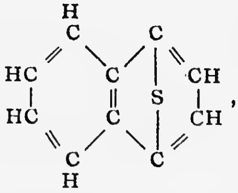
These compounds are produced in the form of lustrous orange or scarlet needles, which cannot be re-crystallised without decomposition. On treatment with water they are decomposed into the original colouring matter and free acid, and a similar result occurs when the hydrochloric acid compounds are heated for some time to 100°.

As is well known the colouring matters here studied form two classes, only one of which combine with acids. Of these, fisetin and maceurin may be taken as types. A third class also exists in which are included gentisein, the colouring matter of gentian root (Tambor, "Inaug. Dissert, Leipsig, 1894") and datiscetin, which is obtained from *Datisca cannabina* (Schunck and Marchlewski, (*Annalen*, cclxxxvii., 261).

	H_2SO_4.	HBr.	HCl.	HI.
Quercetin	$C_{15}H_{10}O_7 \cdot H_2SO_4$	$C_{15}H_{10}O_7HBr$	$C_{15}H_{10}O_7HCl$	$C_{15}H_{10}O_7 \cdot HI$
Rhamnazin	$C_{17}H_{14}O_7 \cdot H_2SO_4$	No action	No action	No action
Rhamnetin	$C_{16}H_{12}O_7H_2SO_4$	,,	,,	,,
Luteolin	$X \cdot H_2SO_4$	,,	,,	,,
Fisetin	$C_{15}H_{10}O_6H_2SO_4$	$C_{15}H_{10}O_6HBr$	$C_{15}H_{10}O_6HCl$	
Morin	$C_{15}H_8O_6H_2SO_4$	$C_{15}H_{10}O_7HBr$	$C_{15}H_{10}O_7HCl$	$C_{15}H_{10}O_7 \cdot HI$
Catechin	No action	No action	No action	No action
Maceurin	,,	,,	,,	,,

80. "*Action of Sulphur on α-Nitronaphthalene.*" By A. HERZFELDER, Ph.D.

When α-nitronaphthalene is heated at about 270° with 25 per cent of sulphur, vigorous interaction takes place, sulphur dioxide being evolved, whilst a black solid mass remains. From this solid an amorphous green substance was isolated which has the formula $C_{10}H_6S$, and the molecular weight 158. It dissolves in the same solvents as sulphur and melts at 155°, with decomposition. It possesses none of the properties of a mercaptan, and gives, on treatment with bromine, αα'-dibromonaphthalene. Its formula it most probably—



and the name αα'-thionaphthalene is proposed for it. The products of bromination, nitration, and sulphonation have been examined.

NOTICES OF BOOKS.

Explosives Act, 1875 (38 *Vict.*, *c.* 17). *Nineteenth Annual Report of Her Majesty's Inspectors of Explosives*; being their Annual Report for the Year 1894. London: Her Majesty's Stationery Office.

THIS report contains matter both of a highly satisfactory and of an alarming nature. As regards the working of the Act no objection can be raised. The total death rate from fire or explosion in manufacture has been reduced to 2, whilst the average for the previous ten years has been 4·6. This improvement has taken place in face of the fact that the number of factories and that of persons employed has decidedly increased, and that in many cases new explosives are being manufactured the risks of which are less well known. The number of factories has risen from 55 (when the Act came into operation) to 130, and that of magazines from 199 to 380. Complaints as to the working of the Act are now becoming very rare, partly in consequence of the fact that foreign countries are introducing laws and regulations concerning explosives greatly based on the British model, but, as a rule, much more stringent.

During the year, four factories have become extinct; seven new factories have been licensed; six applications for new licenses have been received during the year, and there are eight applications outstanding from the previous year.

The growth of the trade since 1875 has been very remarkable.

The following explosives have been added to the authorised list:—Blasting amberite, cordite, collodion cotton, westfalite, von Forster's powder. Compositions containing sulphur in conjunction with chlorate.

The arrangements adopted by the German government for marking all cartridges, so as in case of accidents to identify their origin, have not been adopted, since, though elaborate and costly, the precautions could easily be defeated. But devices for identifying all packages of explosives have been already partially adopted. During the year 192 visits have been made to the factories and infractions or evasions of the Act have been found very rare.

Only one instance has occurred of unlawful entry into a factory and theft of explosives. One instance has occurred of illegal manufacture—blasting cartridges.

In floating magazines additional precautions are recommended. One magazine, at Sancreed, has been struck by lightning, but damage was prevented by the conductor, though the ground was torn up round the earth plates, showing that the resistance to earth was too high. Occasional inspection by a competent electrician is suggested.

The doors of stores for explosives are now very generally protected by iron plating. At the Bryncethin Slate Quarry 4 lbs. of dynamite, 1 lb. of powder, and 16 yards of safety fuse were stolen.

A vessel conveying 20,000 lbs. of dynamite and 10,500 lbs. of blasting gelatin was totally wrecked on rocks at Holy Island; the cargo "was scattered about the rocks and in the water." Steps were immediately taken for its collection and destruction, since there is no reasonable limit to the time during which danger may continue. In a former case at Larn two men were killed by the explosion of some nitro-glycerin remaining from the wreck of the *Essequibo*, nine years previously.

According to the results of a special investigation by Dr. Dupré, re-dipping gun-cotton in fresh acids is a dangerous operation.

The gunpowder explosion on December 13, 1893, at the Waltham Abbey works, has been made the subject of a very careful investigation. The Committee decided that there were very grave defects in the system of discipline and precautions prevailing at Waltham Abbey, and that there is urgent necessity for a comprehensive revision of the regulations, and the adoption of disciplinary measures for their more rigorous enforcement." Of these defects the Committee specify twelve, but they do not wish to regard their list as exhaustive.

A second explosion ensued at Waltham Abbey, May 7, 1894, in connection with the preparation of cordite. There does not appear to have been any defect in the manufacture of the cordite, or of the nitro-glycerin and gun-cotton used as its ingredients. Nor does it appear that the calamity was in any way due to malice.

Accidents have happened with celluloid (xylonite, &c.), but the Inspectors do not see adequate reason for its inclusion in the list of dangerous substances.

There is a list of "scares, and hoaxes, and false alarms." We submit, however, that a part at least of these attempts may have been made in order to lull the authorities and the public into a feeling of false security from which they may some day be fearfully aroused. In one case, at least, the verdict of not guilty returned in the case of an anarchist—an alien—seems to us scarcely justifiable.

Two hoaxers, however, have been each fined £48, which will probably teach them to select other subjects for their jokes.

Meantime genuine outrages have not been entirely wanting. The Greenwich Park accident, of February 18, fortunately avenged itself on its would-be perpetrator, Martin Bourdin. In the case of the attempt against Burwell Church the evidence was insufficient, and as regards the bomb placed at one of the windows of a club at Yarmouth, the perpetrator was never detected.

Two avowed anarchists, Giuseppe Farnara and Polti, were convicted and received the sentences of respectively twenty and ten years penal servitude.

Other attempts were also made concerning the *animus* of which no rational doubt can exist,

Foreign outrages have been more numerous and more deadly, especially in the United States, where, however, much of the mischief seems to have been due to European immigrants. France, Spain, Austria, Italy, and Belgium have been by no means free from the spirit of murderous outrage. In most countries stringent laws have been enacted for the repression of anarchism. It is interesting to learn that the French explosive, mellinite, has still not become exactly known. We may venture to say that had a secret deemed of such national importance been in British hands its composition, with all working details, would ere this have become known to those governments with which there is any possibility of our being involved in war.

Appendices give a table of factories, with a list of the explosives authorised to be made there; a table of explosives authorised to be made in Britain; list of explosives which have passed the tests, but for which no licenses have as yet been taken out; the distribution in counties of factories, magazines, and toy firework factories; also of stores and registered premises; the Order in Council prohibiting fireworks containing sulphur in admixture with chlorates; list of railways whose by-laws have been confirmed; total amount of explosives imported; quantity and value of home-made gunpowder exported.

A special appendix contains a list of the more important outrages and attempts from 1881 to 1894.

CORRESPONDENCE.

"STEEL WORKS ANALYSIS."

To the Editor of the Chemical News.

Sir,—I am sorry that I must beg a little space to reply to Prof. Arnold's letter (Chemical News, vol. lxxi., p. 292). I had decided to pay no attention to Prof. Arnold's criticism in his new work, but a few weeks ago there appeared in a special and important number of the *Iron and Coal Trades' Review* a specially contributed article in which it is stated that "Prof. Arnold, by a modification of Galbraith's volumetric method, obtains reliable results in testing steels for chromium."

Of course, I have no right to ask who wrote the article, but my letter, which also appeared in that journal, has so far elicited no reply.

In his letter he repeats the necessity of diluting the solution. His fears here are contrary to my own experience and to any literature there is on the subject.

He mentions now, however, another objection—"That the large manganese precipitate carries down some chromium with it." Well, we have known that for a long time, but I thought Mr. Stead and I were the first to point that out, in the papers referred to, in the year 1893, and in order to deal with this, I described two remedies —indeed, this was the sole reason of Mr. Stead's modification, and of the precautions mentioned by me; and as the whole teaching of these papers was that there was no fear of non-oxidation of the chromium oxide, it was not difficult to see the unwisdom of using a large excess. But Mr. Stead specially mentions this in his paper of May, 1893. He says: "These results clearly show that the amount of permanganate requires to be carefully regulated," &c.

I do not know to what meeting of two or three years ago Prof. Arnold refers to, where he described a modification in my presence; I was certainly not present at such a meeting. But why did he condemn it in the spring of 1893 if two or three years ago he modified it?

I will not, however, pursue the question further, because if Prof. Arnold remembered "a florid denunciation" of his process by me, and that I declared his process "gave results 50 per cent too high," I can understand his criticisms and have some sympathy with them. I am quite sure, however, if he will make enquiry of those who were present and try to remember what took place, he will acquit me of this.

I did not at the meeting referred to, nor have I at any time, criticised it in any way whatever. Indeed, I had never even tried it; I do not mean by that that I have any opinion about it one way or another. I was simply engaged in the defence of my own method.—I am, &c.,

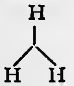
Wm. Galbraith.

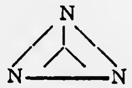
Chesterfield, June 21, 1895.

DIAGRAMMATIC FORMULÆ.

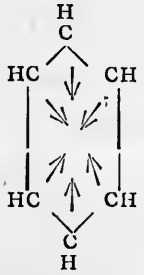
To the Editor of the Chemical News.

Sir,—May I venture to protest against the use of such formulæ as Dr. Brauner proposes for condensed hydrogen and nitrogen, viz.:—





These formulæ, in common with Baeyer's formula for benzene—



are extremely objectionable, inasmuch as they tend to produce a state of mental satisfaction which has no real foundation. Such pseudo-explanatory diagrams are an abuse of graphic formulæ, the legitimate use of which is to connote the chemical—and to some extent the physical—properties of the substances which they are intended to represent. Students are especially liable to be led astray by formulæ like these, which on closs examination are found to be perfectly meaningless.—I am, &c.,

L. Parry, A.R.S.M.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 23, June 10, 1895.

Spectroscopic Examination of the Carbons of the Electric Furnace.—H. Deslandres.—Will be inserted in full.

Physical Properties of Acetylene: Acetylene Hydrate.—P. Villard.—Acetylene is solidified by evaporation in the open air. Its melting-point is −81°. The crystals of solid acetylene, like those of carbonic acid, are absolutely without action upon polarised light. The solubility of the gas has been determined at 0° under the pressure of 4·65 atmospheres. Under these conditions the coefficient of solubility is = 1·6. Acetylene hydrate was first observed by Cailletet in 1871. It is denser than water, and its crystals have no action on polarised light. Its composition may be represented by the formula $C_2H_2,6H_2O$.

Synthetic Formation of Nitro-alcohols.—Louis Henry.—Not adapted for abridgment, and scarcely of sufficient importance for insertion *in extenso*.

Condensation of the Aldehyds and the Saturated Acetones.—Ph. Barbier and L. Bouveault.—From these researches it seems established that among all the acetones, ordinary acetone alone condenses easily with the aldehyds. When the molecular weight of the aldehyds increases, their aptitude for condensation with acetone diminishes, and the chief reaction becomes the condensation of the aldehyd itself.

Causes of the Colouration and of the Coagulation of Milk by Heat.—P. Cazeneuve and M. Haddon.—The yellow colouration of milk on exposure to heat is due to the oxidation of the lactose in presence of the alkaline salts of the milk. Lactose during this oxidation yields acids, especially formic acid, easily detected, the presence of which suffices to explain the coagulation of the milk, as it ensues with any acid. The caseine coagulated is not modified under these conditions, but is merely tinged yellow by brown substances formed at the expense of the lactose.

Active Ethers of the α-Oxybutyric Acids.—Ph. A. Guye and Ch. Jordan.—The authors classify these ethers in five series, and tabulate their optical properties.

Alkaloids of the Fumariaceæ and Papaveraceæ.—M. Battandier.—*Bocconia frutescens* yields fumarine identical with that of *fumaria*, and another alkaloid which is turned to a peach-colour on contact with sulphuric acid, and which he proposes to call "bocconine," traces of a third base having reactions very similar to those of chelidonine, and, lastly, abundance of chelerythrine. Fumarine may occasion an error in the toxicological search for strychnine. The glaucine of Probst contains small quantities of fumarine which gives it the property of taking a violet colour in the cold on contact with sulphuric acid.

A Contribution to the Study of Germination.—Th. Schlœsing, jun.—The author concludes from his experiments that the germination of the grain of wheat and of lupins does not involve any appreciable loss of nitrogen in a gaseous state.

On Amylase.—M. Effront.—An infusion of barley, made in the cold, and then filtered and boiled, triples, and even quintuples, the diastasic power of malt. The value of two malts is proportional to the ratio existing between their saccharifying and liquefying powers.

Employment and the Modus operandi of Chloride of Lime against the Bite of Venomous Serpents.—C. Phisalix and G. Bertrand.—All the experiments of the authors concur in demonstrating that the solution of chloride of lime, advocated against the bite of venomous serpents, has only a local action. It destroys the venom and modifies the tissues, thus obstructing the absorption of the toxic matter. Injections of chloride of lime made at other points than that of the bite have no immunising power, and must be avoided. It is necessary to inject deeply at the very part where the fangs have penetrated.

Revue Universelle des Mines et de la Metallurgie. Vol. xxx., No. 1.

This issue contains no chemical matter.

MISCELLANEOUS.

Study on the Values of the most usual Methods for the Determination of Carbon in Iron.—H. Ledebur.—This extensive paper cannot be reproduced without the six accompanying figures. The author concludes that the two gravimetric methods of Särnström for the determination of the total carbon are the most usual and the most advantageous for use in the metallurgical laboratory.—*Bull. Soc. d'Enc. l'Ind. Nationale*, x., No. 111.

Inspectorship of Alkali Works.—An interesting event took place on the 31st ult., in connection with the retirement of Mr. Alfred E. Fletcher, F.I.C., from the Chief Inspectorship of Alkali, &c., Works, a post which he had held for eleven years. Mr. Fletcher was one of the original Inspectors appointed under the first Alkali Act of 1863, being the only one remaining in office of the original five officials then appointed. Mr. Fletcher was entertained by the Staff at dinner, held at the Hotel Previtali, when presentation was made to him, by his late colleagues, of a silver Monteith bowl with a suitable inscription. Mr. R. Forbes Carpenter, F.I.C., has been appointed by the Local Government Board to succeed Mr. Fletcher as Chief Inspector. Mr. Carpenter joined the Staff in 1882, having subsequently been in charge of the East Lancashire and Yorkshire District.

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END OF VOLUME LXXI.

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

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WILLIAM CROOKES, F.R.S., &c.

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THE CHEMICAL NEWS.

VOLUME LXXII.

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No. 1858.—JULY 5, 1895.

NEW COMBINATION OF ARGON: SYNTHESIS AND ANALYSIS.

By M. BERTHELOT.

The knowledge of the action of carbon disulphide upon nitrogen when submitted to the electric effluve led me to try the same influence upon argon. The experiment has been fully successful; it gives rise to a combination more rapid and complete than that produced with benzene, and not apparently limited like that of phenomena of equilibrium. In each case the mercury intervenes chemically, as I have recognised in my recent experiments.

I operated upon 6·55 c.c. of argon, as pure as possible, and such that benzene, employed once, did not determine (under the influence of the effluve) a direct absorption exceeding nine-hundredths. I brought the gas into contact with liquid carbon disulphide at about 20°, a temperature at which the tension of the sulphide rises to 0·98 metre. This fact has been taken account of.

After three hours of the effluve, under the conditions described in case of nitrogen, the absorption of the argon rose to 11 per cent of its initial volume. After eight hours it increased to 17 per cent.

The gases of the recipient were changed, and a new dose of carbon disulphide was added.

A third reaction of the effluve raised the absorption to 22 per cent; a fourth reaction to 34 per cent; and a fifth reaction to 39 per cent.

The gases of the recipient were changed again; a further dose of carbon disulphide was added, and the experiment was resumed. The total absorption increased then to 56 per cent. The argon represented only 2·9 c.c. An accident prevented me from prolonging this experiment, which had lasted about sixty hours.

But it is scarcely doubtful but that it would have ended in total absorption. It did not appear limited by an inverse reaction, and it is not accompanied at the ordinary pressure by a fluorescence visible in full daylight, and capable of giving rise in diffused light to special spectroscopic rays.

These characters distinguish the absorption of argon by carbon disulphide from its absorption by benzene. In fact, the latter is slower, and is limited by reactions of dissociation which stop the direct action, effected once, at about 9 or 10 per cent with pure argon. Indeed, on separating the unabsorbed argon from its products, we may renew the action, but always with difficulty. After sixty hours, with renewal, I have not gone beyond 16 per cent. Lastly, the absorption of argon by benzene determines the formation of a fluorescent vapour, giving at atmospheric pressure a fine green, visible in full daylight, in which we distinguish among others the rays of the vapour of mercury, *i.e.*, the indication of the presence of a volatile compound of mercury formed in the reaction of argon with the hydrogen carbide. On the contrary, no fluorescence of this kind at this pressure is observed during the absorption of argon by carbon disulphide.

I shall soon return anew to the study of this extraordinary fluorescence. But at present I may mention that it constitutes an essential difference between the combination of argon with the elements of carbon disulphide and its combination with the elements of benzene. Nitrogen gives nothing analogous.

I submitted the product of the reaction to a special examination. The compound naturally contains mercury, but we cannot decide whether this element is associated with argon in one and the same compound. If treated with sodium sulphide it does not give reactions analogous to those of sulphocyanide, except a slight yellow colouration (after acidification) with ferric salts.

I have succeeded in regenerating argon from the compound just mentioned. In this new research I avoided taking the product which had absorbed the first doses of the gas, as it might contain nitrogen if any remained in the argon used for the experiment.

I operated upon the second product, which had absorbed 1·2 c.c. of argon; I submitted this product at once to the action of heat, in the same tubes in which it had been condensed over the mercury after the complete evacuation of the gases, and operating as it had been done in case of carbon disulphide.

Whilst this operation performed on the product of the absorption of nitrogen by carbon disulphide yielded only an insignificant residue, with the product of argon I obtained 0·62 c.c., *i.e.*, equal to about half the volume of the gas absorbed. This number, however, is too low, considering that a very considerable part of the condensed product escapes the action of heat, because of the impossibility of causing the mercury to boil as far as the lower and expanded part of the test-tubes, whereby a portion of the transformed matter is deposited. The contracted part alone is raised to about 500°. Thus the figures given have a merely qualitative meaning, being intended to give some idea of the order of greatness of the phenomena.

I will add that I have caused the condensed product, in the annular intervals of the two tubes, to undergo three successive heatings to dull redness, evacuating each time the gases produced and collecting them again separately. Their gross volume amounted to several c.c. by reason of the regeneration of the carbon disulphide, a circumstance which ensures the most complete elimination of the other gases.

The first heating yielded, after the reaction of the alcoholised potassa and acid cuprous chloride, and final purification by potassa, volume = 0·41 c.c.; the second heating, 0·20 c.c.; the third heating, 0·01 c.c.

The decomposition of heat is thus exhausted in the portion of the substance capable of being heated to dull redness.

To verify if the gas thus regenerated is really argon, I had recourse to the only positive character obtainable in my apparatus, *i.e.*, the production of the fluorescent spectrum developed by benzene at the ordinary pressure. I used effluve-tubes of reduced dimensions, such that 0·40 c.c. of the regenerated gas occupied in the first place a length of 5 or 6 c.m. By operating thus I succeeded, in fact, in obtaining most distinctly, at a pressure bordering upon that of the atmosphere, the green fluorescence characteristic of the compound of argon and benzene. The 0·40 c.c. were reduced thus in eight hours to 0·35 c.c., the absorption taking place with the slowness characteristic of argon, and reaching the same limit. I repeated the same test with 0·12 c.c. of the gas regenerated by the second heating with the same success, and I established in both cases the existence of the specific rays of this fluorescence, developed in diffused light and near the normal pressure.

This experiment seems to me capital, since it demonstrates that argon can enter into combination and be regenerated with its original properties.—*Comptes Rendus*, cxx., p. 1316.

PREPARATION AND PROPERTIES OF PURE MELTED MOLYBDENUM.

By HENRI MOISSAN.

In a former paper we have shown that it is easy to produce cast molybdenum, by heating in the electric furnace a mixture of charcoal and of the oxides of this metal. We shall now give the continuation of our researches on this question.

We must first mention that molybdenum, which is obtained in a pulverulent state by the reduction of the binoxide in hydrogen, was fused by Debray before the blowpipe only in the form of small globules containing 4 to 5 per cent of carbon.

To prepare molybdenum we set out from pure ammonium molybdate, reduced to powder and placed in a crucible of refractory earth, No. 12, capable of containing 1 kilo. The crucible, covered with its lid, is heated for one and a half hours in a Perrot furnace. After cooling, the oxide is a dense powder of a violet-grey, corresponding to the formula MoO_2. One heating yields from 760 to 770 grms. of oxide. This oxide was mixed with sugar-charcoal, in powder, in the following proportions:—

Oxide	300 grms.
Charcoal	30 ,,

In this mixture the oxide is in decided excess compared with the charcoal. The powder is heaped up in a crucible of coke and submitted to the action of an arc produced by a current of 800 ampères and 60 volts for six minutes. We must avoid the complete fusion of the metal, so as to leave a solid layer in contact with the crucible which would be strongly attacked by the liquid molybdenum. Under these conditions we obtain a metal perfectly pure and free from carbon; it is easy in one hour to prepare more than 1 kilo.

If this preparation lasts more than six minutes, the molybdenum obtained is liquefied, corrodes the crucible, becomes carburetted, and we obtain a grey cast metal, very hard and brittle.

Cast Molybdenum.

This cast metal has a specific gravity of 8·6 to 8·9, according to its proportion of carbon. When saturated with carbon it is much more fusible than molybdenum. When rich in carbon it is grey and brittle; at 12·5 per cent of carbon it becomes white, and can be broken up upon the anvil only with difficulty. It presents all the characteristics of the molybdenum studied by Debray. It rapidly dissolves carbon, and abandons it on cooling in the state of graphite, precisely as does cast-iron. Nevertheless, when saturated with carbon it yields a carbide, crystallised in fine needles. Grey cast-molybdenum is very hard; it scratches steel and quartz. When melted, it becomes a very mobile liquid, which can be poured whilst giving bright sparks and abundant fumes of molybdic acid. We have been able to melt and cast ingots of from 8 to 10 kilos. These castings had the following compositions:—

	White.	Grey.
Molybdenum	95·83	92·46
Combined carbon..	3·04, 3·19, 2·54	4·90, 5·50
Graphite	0·00	0·00, 1·71
Slags	0·74, 0·53, c·62	— —

Molybdenum Carbide.

This compound is prepared by heating in the electric furnace molybdenum binoxide with an excess of charcoal. The best proportions are:—Binoxide, 250 grms.; charcoal, 50 grms. The duration of the heating is from eight to ten minutes with a current of 800 ampères and 50 volts. If we use an excess of charcoal it is found in the mass in the state of graphite.

The regulus obtained is of a brilliant white and has a crystalline fracture; it splits readily. It is readily crushed on the anvil, and we may separate from it small elongated prisms of a distinct crystallisation. Its specific gravity is 8·9, and its composition is Mo_2C.

Analysis.

In the various specimens described in this memoir, the molybdenum, after treatment with nitric acid, has been precipitated as mercurous molybdate, and finally determined as bioxide. When the carbide contains no graphite, the carbon was separated by pure dry chlorine, and then determined by combustion in oxygen, according to the weight of carbonic acid collected. According to this method, the portions of carbon are always rather low.

We have obtained the following figures:—

				Theory for Mo_2C.
Molybdenum . ..	93·82	—	—	94·12
Combined carbon .	5 62	5·53	5·48	5·88
Graphite	—	—	—	—
Slags	0·17			
	99·61			

If the carbide contains graphite it is attacked in a flat-bottomed flask traversed by a current of oxygen. The gases evolved pass into a tube filled with copper oxide, the watery vapour is retained in a tube filled with sulphated pumice, and the carbonic acid is fixed in potassa. The increase of the weight of the potassa tube shows the carbonic acid, and, consequently, the carbon. The acid liquid of the flask, after filtration and washing, shows the graphite, and the molybdenum is next determined by mercurous nitrate. This novel method gave as results:—

	9.	10.
Molybdenum	92·60	91·90
Combined carbon	5·15	5·43
Graphite	1·61	1·98

On taking account of the graphite and calculating the proportion of molybdenum to the carbon we find:—

	9.	10.	Theory Mo_2C.
Molybdenum	94·45	94·10	94·12
Combined carbon	5·55	5·90	5·88

Pure Fused Molybdenum.

Pure molybdenum has a specific gravity of 9·01. It is a metal as malleable as iron. It can be easily filed and polished, and forged hot. It does not scratch either quartz or glass. When free from carbon and silicon, it scarcely oxidises in the air below a dull redness. It may be kept for several days unchanged in water, whether ordinary or charged with carbonic acid. In presence of air below dull redness it is covered with an iridescent film, as is steel. About 600° it begins to be oxidised, and yields molybdic acid, which is slowly volatilised.

A fragment of molybdenum heated for some hours in a sloping porcelain tube over an analytical furnace yields, in the upper part of the tube, a felted mass of crystals of molybdic acid. The metal is not covered with any other oxide, and finally disappears, leaving a fine crystallisation of molybdic acid. If heated before the gas-blowpipe, a fragment of molybdenum emits vapours in considerable quantity. If heated before the oxyhydrogen blowpipe, it burns without melting, giving off abundant fumes of molybdic acid and leaving a blue oxide, sparingly fusible. If heated in a current of pure oxygen, it takes fire between 500° and 600°; and if the current is rapid the combustion may continue without the intervention of any extraneous source of heat.

This combustion ensues with intense incandescence, and may serve as a fine lecture experiment.

Melting potassium chlorate attacks molybdenum with violence. The chlorate is melted, and a fragment of molybdenum thrown upon its surface, when it becomes incandescent and revolves upon the surface of the liquid.

The temperature of the reaction rises rapidly, the molybdenum burns with flame, and there escape abundant white fumes of molybdic acid, which remain suspended in the air in the form of white floating filaments. Sometimes the fragment of molybdenum is raised to a temperature high enough to perforate the side of the capsule, which is melted in contact with the metal.

Melting potassium nitrate under similar conditions yields a reaction similar, though less violent, with formation of an alkaline molybdate.

A mixture of molybdenum and lead peroxide heated in a test-tube produces a great liberation of heat and light.

Sulphur has no action at 440°, but hydrogen sulphide at 1200° transforms molybdenum into a bluish grey sulphide, amorphous, having the properties of molybdenite, and leaving, on friction, a black mark upon paper.

Fluorine does not attack molybdenum in fragments, but if the metal is coarsely powdered, there is formed, without incandescence, a volatile fluoride.

Chlorine attacks molybdenum at dull redness, but without incandescence. With bromine, the action takes place at a cherry-red heat, but without great intensity.

Iodine has no action at the temperature of softening glass.

Silver, zinc, and lead fluorides are decomposed, but without the formation of volatile fluorides.

Phosphorus perchloride, if slightly heated, readily attacks molybdenum, forming a volatile chloride, which is easily modified in presence of atmospheric moisture, taking a fine blue colouration.

This reaction is produced with most of the compounds of metallic molybdenum — the oxides, the sulphide, molybdic acid, and the molybdates. It may serve for the rapid detection of metallic molybdenum or its compounds. It is effected in the following manner:—

Into a small test-tube we put a fragment of the substance in question, adding a little phosphorus perchloride, and heating gently. There are formed reddish fumes of molybdenum chloride and oxychloride which condense in a brown ring more or less intense. If the quantity of molybdenum is very slight, the ring may be scarcely visible. It will then be sufficient to expose it to moisture to see it take an intense blue tint, due to the formation of hydrated chloride.

The action of hydracids upon pure molybdenum is almost similar to that which they exert upon cast molybdenum. These experiments, however, have been described by different observers, Bucholz, Berzelius, and Debray. We merely mention that hydrofluoric acid does not attack it, but on adding a drop of nitric acid the action sets in and continues with energy. In presence of a mixture of equal parts of the two acids the solution is complete, and there remains a rose-coloured liquid which, with ferrocyanide, gives an intense red-brown colour, but no precipitate. The mass some hours afterwards coagulates to a jelly.

In a current of nitrogen at 1200°, molybdenum, whether in fragments or in powder, does not form a nitride.

It does not combine with phosphorus at the temperature of melting glass.

Boron combines with molybdenum at the temperature of the electric furnace, yielding an iron-grey melted mass containing cavities lined with prismatic needles.

Under the same conditions, silicon yields a crystalline silicide not fusible before the oxyhydrogen blowpipe.

The action of carbon deserves to arrest our attention for a few moments.

Pure molybdenum, as above described, is a soft metal, which is easily filed and which does not even scratch glass. If we heat a fragment of molybdenum for some hours to a temperature close on 1500° in the midst of a mass of charcoal in powder, it becomes cemented, takes up a small quantity of carbon, and its hardness increases so that it can scratch glass. If we then heat it to 300° and plunge it suddenly into cold water, it is tempered, becomes brittle, and hard enough to scratch rock crystal.

Inversely, if we take cast molybdenum containing 4 per cent of carbon, very hard and brittle, and heat a fragment for some hours with molybdenum binoxide in a lined crucible, it becomes refined, and its surface may then be readily filed and polished.

I attribute this decarburation of the solid cast molybdenum at a temperature very remote from its melting-point to the ready diffusion of vapours of molybdic acid through the metal. I consider that these properties may find applications in metallurgy.

If, in a metal saturated with oxygen, such as is obtained in the first period in the Bessemer converter, we wish to remove this oxygen, we add manganese, which is oxidised more easily than iron, and then passes into the slag (Troost and Hautefeuille). It has been also proposed to employ aluminium, which has given good results, because it is combustible, *i.e.*, because it seizes on the oxygen, but which has the inconvenience of producing solid alumina. I think that molybdenum may be used under the same conditions; it would have the advantage—

1. Of yielding a volatile oxide, molybdic acid, which would be liberated immediately in the gaseous state, stirring up the whole mass.
2. Used in a slight excess it would leave in the bath a metal as malleable as iron, and capable of being tempered along with the latter.

The powder of molybdenum, which it has been attempted to use already, cannot render the same services, because it burns rapidly upon the surface of the bath in contact with the air without having yielded any useful effect.

Analysis of Pure Molybdenum.

	11.	12.	13.	14.
Molybdenum ..	99·98	99·37	99·89	99·78
Carbon	0·00	0·01	0·00	0·00
Slag	0·13	0·28	0·08	0·17

—*Comptes Rendus*, cxx., p. 1320.

ON THE

NEW GAS OBTAINED FROM URANINITE.[*]

(Fifth Note).

By J. NORMAN LOCKYER, C.B., F.R.S.

In a former communication I pointed out the spectroscopic evidence, furnished by the isolation of lines in certain minerals, which indicates that the complete spectrum obtained when bröggerite is submitted to the distillation method is produced by a mixture of gases.

In order to test this view, I have recently made some observations, based on the following considerations :—

1. In a simple gas like hydrogen, when the tension of the electric current given by an induction coil is increased, by inserting first a jar, and then an air-break into the circuit, the effect is to increase the brilliancy and the breadth of all the lines, the brilliancy and breadth being greatest when the longest air-break is used.

2. Contrariwise, when we are dealing with a known compound gas; at the lowest tension we may get the complete spectrum of the compound without any trace of its constituents, and we may then, by increasing the tension, gradually bring in the lines of the constituents, until, when complete dissociation is finally reached, the spectrum of the compound itself disappears.

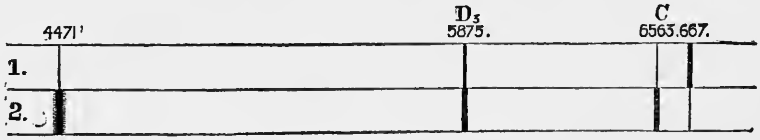

Fig. 1.
Diagram showing changes in intensities of lines brought about by varying the tension of the spark. 1. Without air-break. 2. With air-break.

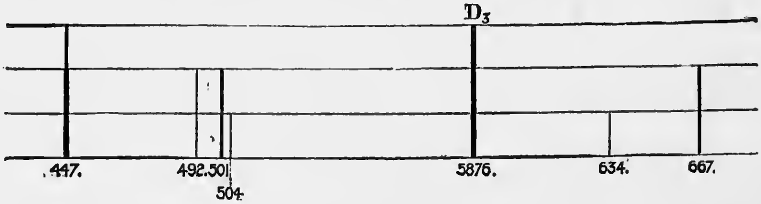

Fig. 2.
Diagram showing order in which lines appear in spectrum of vacuum tube when bröggerite is heated.

Working on these lines, the spectrum of the spark at atmospheric pressure, passing through the gas, or gases, distilled from bröggerite, has been studied with reference to the special lines C (hydrogen), D_3, 667, and 447.

The first result is that all the lines do not vary equally, as they should do if we were dealing with a simple gas.

The second result is that at the lowest tension 667 is relatively more brilliant than the other lines; on increasing the tension, C and D_3 considerably increase their brilliancy, 667 relatively and absolutely becoming more feeble, while 447, seen easily as a narrow line at low tension, is almost broadened out into invisibility as the tension is increased in some of the tubes, or is greatly brightened as well as broadened in others (fig. 1).

The above observations were made with a battery of five Grove cells; the reduction of cells from 5 to 2 made no difference in the phenomena except in reducing their brilliancy.

Reasoning from the above observations, it seems evident that the effect of the higher tension is to break up a compound, or compounds, of which C, D_3, and 447 represent constituent elements; while, at the same time, it would appear that 667 represents a line of some compound which is simultaneously dissociated.

The unequal behaviour of the lines has been further noted in another experiment, in which the products of distillation of bröggerite were observed in a vacuum tube and photographed at various stages. After the first heating, D_3 and 4471 were seen bright, before any lines other than those of carbon and hydrogen made their appearance. With continued heating, 667, 5016, and 492 also appeared, although there was no notable increase of brightness in the yellow line; still further heating introduced additional lines 5048 and 6347.

These changes are represented graphically in the following diagram (fig. 2) :—

It was recorded further that the yellow line was at times dimmed, while the other lines were brightened.

In my second note communicated to the Royal Society on the 8th instant, I stated that I had never once seen the lines recorded by Thalén in the blue, at λ 4922 and 4715.

It now seems possible that their absence from my previous tubes was due to the fact that the heating of the minerals was not sufficiently prolonged to bring out the gases producing these lines.

It is perhaps to the similar high complexity of the gas obtained from clèveite that the curious behaviour of a tube which Professor Ramsay was so good as to send me must be ascribed. When I received it from him, the glorious yellow effulgence of the capillary, while the current was passing, was a sight to see. But after this had gone on for some time, while the coincidence of the yellow line with D_3 of the chromosphere was being inquired into, the luminosity of the tube was considerably reduced, and the colours in the capillary and near the poles were changed. From the capillary there was but a feeble glimmer not of an orange tint, while the orange tint was now observed near the poles, the poles themselves being obscured by a coating on the glass of brilliant metallic lustre.

After attempting in vain for some time to determine the cause of the inversion of D_3 and 447 in various photographs I had obtained of the spectra of the products of distillation of many minerals, it struck me that these results might be associated with the phenomena exhibited by the tube, and that one explanation would be rendered more probable if it could be shown that the change in the illumination of the tube was due to the formation of platinum compounds, platinum poles being used. On May 21st I accordingly passed the current and heated one of the poles, rapidly changing its direction to assure the action of the negative pole, when the capillary shortly gave a very strong spectrum of hydrogen, both lines and structure. A gentle heat was continued for some time and apparently the pressure in the tube varied very con-

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[*] A Paper read before the Royal Society.

siderably, for as it cooled the hydrogen disappeared and the D_3 line shone out with its pristine brilliancy. The experiment was repeated on May 24th and similar phenomena were observed.

ON THE
OCCLUSION OF OXYGEN AND HYDROGEN BY PLATINUM BLACK.*
(Part I.).

By LUDWIG MOND, F.R.S., WILLIAM RAMSAY, PhD., F.R.S., and JOHN SHIELDS, D.Sc., Ph.D.

The authors describe some preliminary experiments on the occlusion of oxygen and hydrogen by platinum sponge and foil, which in general confirm the results obtained by Graham. At most only a few volumes of these gases are occluded by the more coherent forms of platinum.

After giving details of what they consider the best method of preparation of platinum black, they next describe some experiments which had for their object the determination of the total quantity of water retained by platinum black, dried at 100° C., and the amount of water which can be removed from platinum black at various temperatures in vacuo. As the result of these experiments they find that platinum black dried at 100° retains in general 0·5 per cent. of water, and this can only be removed in vacuo at a temperature (about 400°) at which the black no longer exists as such, but is converted at least partially into sponge. At any given temperature the water retained by platinum black seems to be constant. The density of platinum black dried at 100° C. is 19·4, or allowing for the water retained by it at this temperature, 21·5.

The amount of oxygen given off by platinum black at various temperatures was determined. Altogether it contains about 100 volumes of oxygen; the oxygen begins to come off in quantity at about 300° C. in vacuo, and the bulk of it can be extracted at 400° C., but a red heat is necessary for its complete removal. Small quantities of carbon dioxide were also extracted, chiefly between 100—200° C.

In determining the quantity of hydrogen occluded by platinum black the authors have carefully distinguished between the hydrogen which goes to form water with the oxygen always contained in platinum black, and that which is really absorbed by the platinum *per se*. Altogether about 310 volumes of hydrogen are absorbed per unit volume of platinum black, but of this 200 volumes are converted into water, or only 110 volumes are really occluded by the platinum. Part of it can be again removed at the ordinary temperature in vacuo; by far the larger portion can be extracted at about 250—300° C., but a red heat is necessary for its complete removal. The amount of hydrogen absorbed by platinum is very largely influenced by slight traces of impurity, probably grease or other matter which forms a skin over the platinum.

Platinum black in vacuo absorbs a certain quantity of hydrogen. On increasing the pressure of the hydrogen up to about 200—300 m.m. a further quantity is absorbed, but after this pressure is almost without effect. By increasing the pressure from one atmosphere up to four and a half atmospheres, only one additional volume of hydrogen was absorbed. On placing platinum black charged with oxygen in an atmosphere of oxygen, and increasing the pressure to the same extent, eight and a half additional volumes were, however, absorbed.

Platinum black charged with hydrogen and placed in an atmosphere of hydrogen kept approximately at atmospheric pressure, and platinum black charged with oxygen and confined in an atmosphere of oxygen behave quite differently when heated. In the former case hydrogen is immediately expelled on raising the temperature, whilst in the latter case oxygen is steadily absorbed until a temperature of about 360° C. (the temperature of maximum absorption) is reached, when, on further heating, oxygen begins to come off again.

Incidentally it was noticed that mercury begins to combine with oxygen at 237° C., and that a mixture of platinum black and phosphorus pentoxide absorbs oxygen at a high temperature, probably with the formation of a phosphate or pyrophosphate.

In the discussion of the results special reference is made to the work of Berliner and Berthelot, and it is pointed out that there is not sufficient evidence for the existence of such chemical compounds as $Pt_{30}H_3$ and $Pt_{30}H_2$. Moreover, the authors are of opinion that the heats of combination of hydrogen and platinum as determined by Berthelot and Favre are valueless, and that the heat which they measured is due, for the most part if not entirely, to the formation of water by the oxygen always contained in platinum black. It has yet to be *proved* that the absorption of hydrogen by pure platinum black is attended by the evolution of heat, and as regards the formation of supposed true chemical compounds, solid solutions, or alloys, the authors prefer to wait until sufficient data have been accumulated for an adequate inquiry before coming to any definite conclusion.

ON THE
FORGING OF FLAT CRUCIBLE STEEL INGOTS FOR TOOL MANUFACTURE.

By SERGIUS KERN, M.E.

In the Chemical News (lxxi., p. 187) I gave a description of my system of casting crucible steel ingots. I may add that the forging of ingots is going well, and the loss through piping is remarkably small. Capt. Trouchanoff, manager of the forge of the New Admiralty, St. Petersburg, thus reports about my system:—

"In many cases, during the manufacture of various tools at works, having for such work crucible steel ingots, it is much preferable to use flat ingots, cast by Mr. Kern's system."

St. Petersburg, June 2, 1895.

NOTE ON "STANDARD" ACID SOLUTIONS.

By H. DROOP RICHMOND.

Dr. Perman and Mr. John describe (Chemical News, lxxi., 296) a new method for standardising solutions. Seeing that it has been used for at least eight years, and has been exhaustively studied by Rimbach (*Ber.*, xxvi., 164), who even used the method of titration of borax with acid, methyl orange being employed as indicator, for the determination of the atomic weight of boron, it is not correct to call it a new method.

The process is certainly very convenient, and much more accurate than the results of Messrs. Perman and John would indicate—*e.g.*, a difference between duplicates of 0·4 per cent is shown; certain precautions are, however, necessary, to which the authors have not drawn attention. From the very fact of the method being described as new, it is evidently not so well known as it should be, and consequently no excuse need be offered for describing the necessary precautions.

It does not do to trust to the borax having the composition $Na_2B_4O_7.10OH_2$. The water of crystallisation should be estimated at the time of weighing out the borax; half-an-hour's ignition in a muffle is usually necessary to drive off all the water.

Commercial methyl-orange sometimes contains an

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* bstract of a paper read before the Royal Society.

objectionable brown colouring-matter, which can, however, be removed by one or two crystallisations from alcohol.

The solution of the borax should not be too strong; about 20 c.c. of water for each 1 grm. is convenient. If too large a proportion of neutral salts be present, the delicacy of the end reaction is impaired; this is probably the reason for the difference of 0·4 per cent in Messrs. Perman and John's results.

An excellent method of preparing standard sulphuric acid is to weigh a quantity of acid of known density (best about 96 per cent H_2SO_4), and dilute to a definite volume. The excellent work of Pickering (*Journ. Chem. Soc.*, lvii., p. 64) has given us data for the calculation of the strength of sulphuric acid from the density with great exactitude.

It must be remembered that, whether the sulphuric acid is weighed, or titrated with borax, or estimated with barium chloride, that the strength of our acid is expressed in terms of the actual sulphuric acid present; when we come to use this acid in practice, employing, as is very frequently the case, phenolphthalein as indicator, we have not only the acidity of the sulphuric acid, but also that of the dissolved carbonic acid, entering into the reaction. We are usually very careful in keeping our alkali solutions free from carbonates (where they are of minor importance, as the alkali solution is always standardised against acid solution), while we utterly neglect all precautions for keeping our acid solutions free from carbonic acid.

The atomic weight of boron seems to be from the determinations of Ramsay and Aston, and Rimbach, who both used borax, 10·95, and, adopting this and the atomic weights given by Clarke for sodium, oxygen, hydrogen, and sulphur and chlorine, 1 grm. of anhydrous borax is equal to 0·48575 grm. sulphuric acid and 0·36115 grm. hydrochloric acid.

THE DETERMINATION OF WATER IN COMMERCIAL SAMPLES OF SULPHATE OF AMMONIA.

By JOHN HUGHES, F.I.C.

It is not generally usual to state the percentage o water present in commercial samples of sulphate o ammonia.

Occasionally chemists are asked to do so, also to state the amount of acidity, and in such cases the figures are given; but usually only the percentage of nitrogen equal to ammonia is reported.

The writer thinks that it would be desirable and useful that the percentage of water lost at 212° F., and the acidity expressed as H_2SO_4, should always accompany the figures for nitrogen and ammonia on the certificate.

Sulphate of ammonia, when ground up in a mortar, rapidly loses moisture in a hot dry atmosphere.

Consequently, in order to make a correct report on the percentage of nitrogen contained in the sulphate of ammonia in its natural state as received, it becomes necessary to make two water determinations. One in the sample as turned out in its rough damp state before grinding, and one in the finely ground portion prepared for the purposes of analysis; the analytical results being afterwards calculated into the natural state as received and reported accordingly.

The question of water really is a most important one, bearing in mind the commercial value of the material and the fact that every 1 per cent of water lost represents an increase of 0·25 per cent of ammonia.

It is true that the introduction of centrifugal machines has largely reduced the proportions of water and acidity in the sulphate of ammonia as sent out; but there is still sufficient difference between the dampness, respectively at the top and the bottom of the bags, to make the sampling a matter of great importance.

The following twelve samples, representing one delivery of yellow sulphate of ammonia, were furnished the writer by a large London manure firm, six bags being selected, and samples drawn respectively, from the top and bottom of each.

The proportions of water and acidity were then carefully determined as above suggested, a weak solution of litmus being employed as indicator in titration for acidity.

Top Samples.

	Water as received.	Water as analysed.	Water lost during preparation.	Free acid calculated as H_2SO_4.
1	1·98	1·26	0·72	0·97
2	1·81	1·42	0·39	0·63
3	1·59	1·20	0·39	0·65
4	0·87	0·48	0·39	0·81
5	1·12	0·50	0·62	0·79
6	1·32	0·72	0·60	1·03
Average ..	1·45	0·93	0·52	0·81

Bottom Samples.

	Water as received.	Water as analysed.	Water lost during preparation.	Free acid calculated as H_2SO_4.
1	2·62	1·64	0·98	1·24
2	2·65	1·94	0·71	0·81
3	2·53	1·76	0·77	0·80
4	3·14	2·12	1·02	1·22
5	1·97	1·24	0·73	0·71
6	2·39	1·84	0·55	1·07
Average ..	2·55	1·76	0·79	0·97

It will be noticed that the differences are considerable' the top samples being much drier than the bottom ones, in No. 4 the difference being as much as 2·27, representing 0·56 ammonia; and the water lost during preparation amounting in some cases to over 1 per cent, representing 0·25 ammonia.

Of course this loss during preparation will vary with the degree of grinding, the time exposed, and the temperature and humidity of the atmosphere.

The following figures in seven other samples, each representing a different delivery and analysed at a different time, will serve to indicate the variation that may be expected:—

Colour.	Water as received.	Water as analysed.	Water lost during preparation.	Free acid calculated as H_2SO_5.
White	2·20	1·80	0·40	0·29
Yellow.. ..	1·94	1·50	0·44	0·31
Yellow.. ..	2·31	2·06	0·25	0·15
Grey	2·96	2·74	0·22	0·38
White	1·70	1·10	0·60	0·15
White	1·90	1·40	0·50	0·23
White	1·89	1·32	0·57	0·25
Average ..	2·13	1·70	0·42	0·25

The amount of acidity is of importance, because if not excessive, say not more than 0·5 per cent, the sulphate of ammonia can safely be shipped in double bags instead of in the more expensive casks which were formerly used.

If the certificate of the analyst contains information as to the percentage of water and acidity, in addition to the figures for nitrogen equal to ammonia, the identity of the sample with the bulk can be more readily established than when the figures for ammonia only are stated.

In a paper published in the Chemical News (lxii., p. 325) the writer drew attention to the importance of stating the percentage of water when reporting on the quality of wool waste, and pointed out that the omission to do so, and to state the percentage of nitrogen for the sample as received, had no doubt caused the serious differences between analysts, which up to that date was of frequent occurrence, but which since then have disappeared.

He trusts that this communication may be received by analysts in a similar favourable manner.

79, Mark Lane, London, E.C.,
June 20, 1895.

ON THE NATURE AND COMPOSITION OF THE COMMERCIAL RUSSIAN KEROSENE.

By J. ALFRED WANKLYN and W. J. COOPER.

In December, 1893, and in January, 1894, in the *Philosophical Magazine* and in the CHEMICAL NEWS, the announcement was made that, by most persistent and methodical fractionation, a homologous series of hydrocarbons had been separated into its terms, and that its terms differed from one another, not by the common increment 14, but by the common increment 7. In following papers we have disclosed that the hydrocarbons in question are the hydrocarbons existing in mixture in the commercial Russian kerosene, and have published further details.

On the present occasion we publish a tabular *resumé* of the work. The hydrocarbons of this series we have named keroses, and in the table the Roman numeral expresses the number of atoms of carbon (the atomic weight of carbon being 6) in the molecule of the kerose.

We have obtained an acetic compound of almost every individual kerose, one molecule of kerose being united with one little molecule of acetic acid. The preparation of such compounds was described in the CHEMICAL NEWS of May 24 (vol. lxxi., p. 250).

		V. D.		Sp. gr. at 15·5° C.	Boils at °C.	Percentage of Hydrocarbon in Acetic K.	
		Theory.	Found.			Theory.	Found.
A*y*	xiii.	3·144	3·192	0·7350			
A*z*	xiv.	3·386	3·43	0·7460	85	62·04	62·33
A*a*	xv.	3·63	3·69	0·7510	96·5	63·63	62·75
A*b*	xvi.	3·87	3·91	0·7576	106	65·12	64·48
B	xvii.	4·11	4·08	0·7606	116·5	66·48	65·9*
B*b*	xviii.	4·35	4·36	0·7711	127	67·74	67·84
B*c*	xix.	4·59	4·59	0·7768	138	68·91	69·06
C	xx.	4·84	4·84	0·7843	148	70·00	69·70
D	xxi.	5·08	5·02	0·7975	158	71·01	70·94
D*d*	xxii.	5·32	5·20	0·8057	168	71·96	72·00*
D*e*	xxiii.	5·56	5·51	0·8090	176	72·87	72·99
E	xxiv.	5·80	5·77	0·8185	186	73·68	74·01
F	xxv.	6·04	6·08	0·8240	197	74·47	74·64
F*f*	xxvi.	6·28		0·8255	205	75·21	75·28
G	xxvii.	6·52	6·53	0·8270	214	75·90	77·02
G*g*	xxviii.	6·77	6·82	0·8287	222	76·56	77·31
H	xxix.			0·8338	230	77·18	77·53
H*h*	xxx.			0·8392	237	77·77	77·53
I	xxxi.			0·8430	246	78·34	78·34*
K	xxxii.			0·8470	253	78·87	79·43
L	xxxiii.			0·8520	260	79·38	79·95
M	xxxiv.			0·8560	267	79·87	79·83
N	xxxv.			0·8590	274	80·33	80·63*
O	xxxvi.			0·8603	280	80·77	80·55

* Mean.

Z residue, dark coloured liquid, sp. gr. 0·880, amounting to about 13 per cent of the total kerosene.

The circumstance that the specific gravity of the liquid kerose always rises as the molecule increases in weight will be noted. This rise is small, but invariable, and affords an argument in favour of there being substantially only one hydrocarbon series present in the Russian kerosene of commerce. Apparently, however, the rise (though it always occurs) is not always equal in extent.

The boiling-points of the keroses must be looked upon as to some extent provisional. We are in possession of the liquids and have not used them up in making the acetic compounds, and we purpose to re-determine the boiling-points.

A REFORM IN CHEMICAL, PHYSICAL, AND TECHNICAL CALCULATIONS.

By C. J. HANSSEN, C.E.

(Continued from p. 309).

The Dynamic Equivalent of Heat.

IF 1 cbm. hydrogen of atmospheric pressure and 273° N. absolute temperature is heated to 546° N. absolute (273° increase of temperature), it expands to 2 cbm. of 1 atmosphere pressure; it would, enclosed in a cylinder with movable piston of 1 sqr. m. area, by expanding, move the piston 1 m. against the pressure of the atmosphere; and, consequently, as atmospheric pressure upon 1 sqr. m. is =10330·442 kg., perform 10330·442 m.kgr. of work.

To heat 1 cbm. of hydrogen 273° N., is required—

At constant pressure	$273^\circ \times 17/56$ cal.
At constant volume	$273^\circ \times 12/56$,,
The difference	$273^\circ \times 5/56$ cal. =

$1365/56 = 24\frac{3}{8}$ calor. = 24·375 cal. has performed 10330·442 m.kgrs. of work; consequently,—

$$1 \text{ cal.} = \frac{10330{\cdot}442}{24{\cdot}375} = 423{\cdot}813 \text{ m.kgs.}$$

Exactly the same result do we get by calculating with oxygen, nitrogen, or other simple gases, and likewise with CO and with air; but, by making the calculation with a compound gas which, in combining, has contracted its volume, the result is *apparently* different.

For *carbon dioxide* (of which 1 cbm. contains $1\frac{1}{2}$ cbm. of simple gases, are required—

At constant pressure	$273^\circ \times 51/112$ cal.
At constant volume	$273^\circ \times 36/112$,,
The difference	$273^\circ \times 15/112$ cal. =

$4095/112 = 36\frac{9}{16}$ calor., moves the piston 1 m., and performs 10330·442 m.kgrs. of work. This compound gas has consequently absorbed exactly $1\frac{1}{2}$ times as much heat as the simple gas, to perform the same amount of work, but in this case, $\frac{1}{3}$ of the $36\frac{9}{16}$ cal. $= 12\frac{3}{16}$ cal., is absorbed to counteract the chemical affinity which contracted 1 cbm. O and $\frac{1}{2}$ cbm. C into 1 cbm. CO_2, and the remaining $\frac{2}{3} \times 36\frac{9}{16} = 24\frac{3}{8}$ calor. perform the same amount of dynamic work as in the first case. The same calculation made with many other gases, gives, with absolute accuracy, the same result: 1 calor. = 423·813 m.kgrs.

Water evaporates in vacuum at $219\frac{3}{8}^\circ$ N. absolute ($-53\frac{5}{8}^\circ$ N.), because, by very careful investigation of Regnault's experiments on evaporation of water, the author finds that in all cases, from the highest to the lowest temperature,—

$$\frac{W \times T}{P} = 219\tfrac{3}{8}$$

Here T denotes the absolute temperature of the steam (°N.), W the weight of the steam (kgr. per cbm.), and P the absolute pressure of steam in atmospheres; and for all weights, pressures, and temperatures of steam ascertained by those experiments, the coefficient—

$$219{\cdot}375 = 219\tfrac{3}{8} = \underline{1755}$$

is the result. For every known pressure and weight of steam we consequently find the corresponding absolute temperature, T, by the equation—

$$T = \frac{1755\ P}{8\ W} = x^\circ \text{ N. absolute.}$$

Aëriform substances increase in weight in *inverse* proportion to their absolute temperature; consequently, vapour of water (steam) of 1 atmosphere and 273° N. absolute, of which 1 cbm. weighs 45/56 kg., would weigh 56/56 kg. (= 1 kg.) if cooled, as proportion—

$$56 : 45 = 273^\circ \text{ absolute} : 219\tfrac{3}{8}^\circ \text{ N. absolute.}$$

If at $219\frac{3}{8}^\circ$ N. absolute 1 cbm. steam of 1 atmosphere weighs 1 kg., then 1 cbm. of 0·00000001 atmosphere must weigh 0·00000001 kg. If we insert these values for P and W in the equation, we find the temperature—

$$T = \frac{1755 \times 0{\cdot}00000001 \text{ atm.}}{8 \times 0{\cdot}00000001 \text{ kg.}} = 219\tfrac{3}{8}^\circ \text{ N. abs.} = -53\tfrac{5}{8}^\circ \text{ N.}$$

where water will commence to evaporate in absolute vacuum. By increasing the temperature, the pressure of steam increases in the following ratio:—

Atmospheres.		Absolute. °N.	°N.
0·00000001		$219\frac{3}{8}$	$= -\ 53\frac{5}{8}$
0·0000001		$220\frac{13}{27}$	$= -\ 52\frac{14}{27}$
0·000001	$220\frac{13}{27} + (\frac{128}{27} \times 1{\cdot}5^0) =$	$225\frac{2}{9}$	$= -\ 47\frac{7}{9}$
0·00001	$225\frac{2}{9} + (\frac{128}{27} \times 1{\cdot}5^1) =$	$232\frac{1}{3}$	$= -\ 40\frac{2}{3}$
0·0001	$232\frac{1}{3} + (\frac{128}{27} \times 1{\cdot}5^2) =$	243	$= -\ 30$
0·001	$243 + (\frac{128}{27} \times 1{\cdot}5^3) =$	259	$= -\ 14$
0·01	$259 + (\frac{128}{27} \times 1{\cdot}5^4) =$	283	$= +\ 10$
0·1	$283 + (\frac{128}{27} \times 1{\cdot}5^5) =$	319	$= +\ 46$
1·0	$319 + (\frac{128}{27} \times 1{\cdot}5^6) =$	373	$= +100$
10·0	$373 + (\frac{128}{27} \times 1{\cdot}5^7) =$	454	$= +181$
100·0	$454 + (\frac{128}{27} \times 1{\cdot}5^8) =$	$575\frac{1}{2}$	$= +302\frac{1}{2}$

By calculating the temperatures due to 83 intermediate pressures, and of these construct a diagram, the author obtained a curve, which agrees well with Regnault's experiments; in fact, so well that the small deviations must be caused by *experimental* errors.

The specific heat of liquid water, as usually taken, $= 1$; the specific heat of ice (which is condensed H_2O at constant volume), of vaporised water (steam), and of H_2O gas is $= 0{\cdot}4$. Melting 1 kgr. of ice absorbs $79\frac{1}{4}$ calors, which become latent. Evaporating 1 kgr. of liquid water absorbs $8 \times 79\frac{1}{4} = 634$ calor., which become latent, minus 0·1 cal. per °N. absolute temperature of the steam generated.

Heat required to Melt Ice, Vaporise and Decompose Water.

1 kgr. solid H_2O (ice) at absolute zero of temperature (0° abs.) contains no heat;—

Heated to 273° abs. (+0° N.) it contains $273 \times 0{\cdot}4$ cal.	=	109·20	calor.
Latent heat of liquefaction of ice	=	79·25	„
Total heat in 1 kgr. *liquid* water of 273° N. abs. (0° N.)	=	188·45	„
Latent heat of evaporation per 1 kgr. liquid water of 273° N. absolute converted into vapour of 273° N. abs., 634 cal. − (273° × 0·1 cal.)	=	606·70	„
Total heat in 1 kgr. steam of 273° N. absolute (0° N.)	=	795·15	„

Heat required to evaporate 1 kgr. liquid water of 273° N. absolute (0° N.) into steam of atmospheric pressure and 373° N. absolute (100° N.)—

Latent heat of evaporation, 634 cal. − (373° × 0·1 cal.)	=	596·70	calor.
1 kgr. steam heated 100° N. and 0·4 cal.	=	40·00	„
To convert 1 kgr. water of 0° N. into steam of 100° N. requires		636·70	„

To evaporate 1 kgr. water of 273° N. absolute into steam of 10 atmospheres pressure and 454° N. absolute (181° N.), is required:—

Latent heat of evaporation 634 cal. − 454° × 0·1 cal)	=	588·60	calor.
1 kgr. steam heated 181° N. and 0·4 cal.	=	72·40	„
To convert 1 kgr. of water of 273° N. absolute (0° N.) into steam of 181° N. requires		661·00	„

These examples, which also hold good for lower and higher pressures, show that although $\frac{12}{30} = 0{\cdot}4$ calor. are required to raise the temperature of 1 kgr. saturated steam 1° N., only 0·3 calor. are to be supplied from outer sources of heat, while 0·1 calor., taken from the 634 calor. latent heat of evaporation, is converted into sensible heat or temperature.

These 0·3 calor. are, in the process of evaporation, applied thus:—

$\frac{1}{9} = 10/90$ calor. per 1° N. is used to overcome atmospheric resistance.

$\frac{1}{18} = \ 5/90$ calor. is used to overcome chemical affinity of H and O.

$\frac{2}{15} = 12/90$ calor. is used to overcome physical cohesion of atoms.

27/90 calor. = 0·3 calor per 1° N. to be supplied from outer sources of heat.

The $79\frac{1}{4}$ calor. + 634 calor = 713·25 calor. latent melting and evaporating heat required to evaporate 1 kgr. ice 0° N. abs., decrease 0·3 calor. for every 1° N. temperature above absolute zero; consequently, the absolute temperature, where water is converted into permanent H_2O gas, is found by proportion:—

$$0{\cdot}3 \text{ cal.} : 713 : 25 \text{ cal.} = 1^\circ \text{ N.} : 2377{\cdot}5^\circ \text{ N. absol.}$$

Heating 1 kgr. H_2O at constant pressure 1° N. requires $\frac{17}{30}$ calor.; consequently, raising the temperature from 0° absolute to 2377·5° N. absolute requires—

$$2377{\cdot}5^\circ \text{ N.} \times \tfrac{17}{30} \text{ cal.} = 1347\tfrac{1}{4} \text{ calor.,}$$

which is equal to—

$$(1+8+8) \times 79\tfrac{1}{4} \text{ cal.} = 17 \times 79\tfrac{1}{4} \text{ cal.} = 1347\tfrac{1}{4} \text{ calor.}$$

Water Decomposed into Simple Hydrogen and Oxygen Gas.

If we heat 1 kgr. of solid water (ice), of 0° N. absolute, to $1\frac{1}{2} \times 2377\frac{1}{2}^\circ$ N. absolute $= 3566\frac{1}{4}^\circ$ N. absolute, we have brought it to the temperature where the molecules of H_2O decompose into simple H and O gas. To heat 1 kgr. of solid water of 0° N. absolute to this temperature are required—

$$3566\tfrac{1}{4}^\circ \text{ N.} \times \tfrac{17}{30} \text{ cal.} = 2020\tfrac{7}{8} \text{ calor.}$$

But in order actually to split the H_2O molecules into simple hydrogen and oxygen gas of $3566\frac{1}{4}^\circ$ N. absolute temperature, are required per 1 kgr.:—

$$2 \times 2020\tfrac{7}{8} \text{ calor.} = 4041\tfrac{3}{4} \text{ calor.,}$$

which is equal to—

$$3 \times (1+8+8) \times 79\tfrac{1}{4} \text{ cal.} = 3 \times 17 \times 79\tfrac{1}{4} = \\ = 51 \times 79\tfrac{1}{4} = 4041\tfrac{3}{4} \text{ calor.}$$

By this operation, the 1 kgr. of ice of 0° N. absolute is dissolved into $\frac{1}{9}$ kgr. of hydrogen and $\frac{8}{9}$ kgr. of oxygen, which, at that temperature ($3566\frac{1}{4}^\circ$ N. absolute), are = 634/39 cbm. hydrogen and 317/39 cbm. oxygen = total 951/39 cbm. = $24\frac{5}{13}$ cbm. of simple gases of $3566\frac{1}{4}^\circ$ N. absolute and atmospheric pressure.

As dissolving 1 kgr. of ice of 0° N. absolute temperature into its components requires $4041\frac{3}{4}$ calor., it follows that the combustion of $\frac{1}{9}$ kgr. hydrogen with $\frac{8}{9}$ kgr. oxygen (which form 1 kgr. of water), must likewise develop $4041\frac{3}{4}$ calor.; and, consequently, the combustion of 1 kgr. of H with 8 kgrs. of O, forming 9 kgrs. of water, will produce:—

9 kgrs. × $4041\frac{3}{4}$ calor. absolute =	36375·75	calor. total heat
9 kgrs. of water of 273° N. abs. contain 9 × 188·45 cal. =	1696·05	„

Consequently—

1 kgr. hydrogen burnt with oxygen produces	34679·70	„

if the initial temperature of the gases has been 273° N. absolute, and the products of combustion are cooled down to that temperature; and the temperature of combustion of H with O is $3566\frac{1}{4}^\circ$ N. absolute, and $3566\frac{1}{4}^\circ - 273^\circ = +3293\frac{1}{4}^\circ$ N.

Pressure exerted by Freezing Water.—This pressure the author finds to be $= 1904$ atmospheres.

Water hermetically enclosed in a strong vessel remains liquid at $-24°$ C. (249° C. absolute), as proved by M. Bousingault's experiment; and probably it remains liquid at all lower temperatures down to $219\frac{3}{8}°$ N. absolute if expansion is absolutely prevented.

(To be continued.)

3, Valdemarsgade, Copenhagen, V.
May 6, 1895.

SPECTROSCOPIC STUDY OF THE CARBONS OF THE ELECTRIC FURNACE.

By H. DESLANDRES.

H. Moissan has recently announced (*Comptes Rendus*, cxix., p. 1245) that the carbons of the arc in his electric furnace are purified by the passage of currents of great intensity, and are thus freed from the foreign matters which they always contain in notable proportion.

We know that it is very difficult to purify charcoal by chemical means. This property of the electric furnace is therefore important, and in particular it interests spectroscopists who in their researches of qualitative analysis often employ electrodes of carbon as pure as possible. I have thus been led to a special study of the carbons of the electric furnace, to ascertain on the one hand their value in analysis, and on the other to determine the complete spectrum of pure carbon.

Moissan having placed at my disposal two carbon poles, a positive and a negative (length of 0·20 metre and thickness of 0·05 metre), which had served in his experiments, I took from each pole small portions of charcoal at variable distances from the arc (0·15, 0·10, 0·05, and 0·01). Now the specimens the most remote from the arc still showed the rays of the ordinary impurities of charcoal, *i.e.*, the alkaline and earthy-alkaline metals, with copper, iron, and silicon; but on approaching the arc, the rays of the impurities gradually diminished and finally disappeared, excepting only the rays of calcium, which, although much reduced, are still visible; this fact being due to the proximity of the sides of the furnace consisting of lime. These sides are themselves volatilised by very intense currents.

This purification of carbon seems to depend on a purely physical cause; the foreign matters, much more volatile than the carbon, are thrown off in the state of vapour. In fact, the purest parts of the two poles are the caps ("mushrooms," as the author calls them), which are formed at the negative pole of transportation from the positive pole to the opposite pole. With one of the caps the following spectrum of carbon has been obtained, containing fewer rays than the similar spectrum published by Liveing and Dewar, Hartley and Adeney, Eder and Valenta:—

Intensities.	Wave-lengths.	
8	426·70	
5	392·17	
4	391·97	?
2	316·83	
1	316·57	
2	299·34	
1	296·77	
8	283·75	
8	283·69	
4	274·75	
3	264·12	
8	251·19	
8	250·79	
10	247·88	
8	229·70	

—*Comptes Rendus.*

RELATION BETWEEN VALENCE AND ATOMIC VOLUME.

By HOLLAND CROMPTON.

In these (*Berichte*, xxvii., p. 2178—compare also *Zeit. f. Anorg. Chemie*, viii., p. 127) J. Traube shows the existence of a relation between valence and atomic volume, and that the "change of valence of an elementary atom is mostly attended with a change of the atomic volume," the atomic volume here in question being the atomic solution volume.

In a memoir which I have recently submitted to the Chemical Society of London, I showed that there exists an intimate relation between the molecular (or atomic) latent heat of fusion, ρ, and the valences of the atoms present in the molecule, so that it is possible, by means of certain simple rules laid down in the memoir, to deduce from the valences a number ΣV, such that $\rho T_0 = C\Sigma V$, where T_0 signifies the melting-point in absolute degrees of temperature, and C is a constant which has the same value for all substances. The connection of the latest heat of fusion with the valence leads to the following confirmation of Traube's results:—

In the year 1870 Goldberg (*Compt. Rend.*, lxx., p. 1349) established the following relation between the vapour-pressure p' of a solution of the melting-point T in absolute temperature, and the vapour-pressure p of the solvent of the melting-point T_0:

$$ln\frac{p}{p'} = \frac{\rho}{R}\ \frac{T_0 - T}{T_0\ T},$$

where R is the constant of the Boyle-Gay Lussac equation. It may now be shown, thermo-dynamically (Nernst, "Theoret. Chemie, p. 125), that if P is the osmotic pressure of a solution in which a change of volume dv is effected by the removal of dx grms. of the solvent, the equation holds good:—

$$P = \frac{dx}{dv} RT\, ln\frac{p}{p'}.$$

If this formula is combined with that of Goldberg, we have—

$$\frac{P}{T_0 - T}\ \frac{dv}{dx} = \frac{\rho}{T_0} = C\Sigma V.$$

Here dv/dx is the volume occupied by 1 mol. of the solvent in the given solution; therefore the molecular volume of the solvent, or that part of the solution which separates out at the point of fusion, is the dissolved salt in solutions near on saturation for which Traube's relation is applicable. Consequently the molecular volume of a salt is a function of the valences of the atoms forming the molecule.—*Berichte*, xxviii., No. 2, p. 148.

EXAMINATION OF BLOOD-PIGMENT AS TO ITS POWER OF ABSORBING THE VIOLET AND ULTRA-VIOLET RAYS.*

By H. GRAEBE.

As the source of light, the author used in part sunlight and in part the light of the electrical spark, the spectrum of which extends to six or seven times the length of the visible spectrum beyond H. The induction current of a Ruhmkorff apparatus was excited by four Bunsen elements, and served to charge a battery of nine Leyden jars. In most of the investigations an iron and a copper pole were used. The division of the spectrum thus obtained was effected by comparison with the photograph of the spectrum of a spark obtained under exactly the same

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* An Inaugural Dissertation at Dorpat, 1892.

conditions, and which had passed between the poles of an alloy of lead, tin, and cadmium; the wave-lengths of the lines of the latter spectrum were obtained from a paper of Hartley's (*Phil. Trans.*, 1885). As the achromatic collimator lens generally employed for photographs extending beyond H (consisting of a plano-convex lens of calcareous spar and a bi-convex quartz lens) was not at hand, the author used a chromatic quartz lens, which certainly showed only one part of the spectrum distinctly, whilst the other parts could be successively adjusted sharply by a corresponding rotatory movement of the quartz prism. The displaceable slit of the spectroscope constructed by the author was placed, accurately centred, at double the focal distance of the lens. Immediately behind the lens was the prism, so adjusted on a movable axle that its requisite rotation could be regulated by means of a scale and index. As troughs there were used vessels of rock crystal, with plane parallel sides.

For the proofs there were used the Lumière's ordinary silver-bromide plates. The time of exposure varied according to the state of the sunlight, from 30 to 120 seconds, and for the light of the spark between 200 and 100 electric discharges. The proofs were developed with iron oxalate, and fixed with a 15 per cent solution of hyposulphite.

Soret (*Comptes Rendus*, xcvii., 1269) had observed the absorption of blood in the violet, and mentions also two absorption bands, "one of which, at Cd_{12}, is probably due to hæmoglobine, whilst the other, at Cd_{17}, is evidently produced by the serum." D'Arsonval has also recognised the absorption band of oxyhæmoglobine in the violet. The author, whilst making use of these former researches, has studied, by the aid of photographs, the absorptions of oxyhæmoglobine, hæmoglobine, methæmoglobine, cyanmethæmoglobine, sulphomethæmoglobine, carbonic oxide hæmoglobine, hæmatine, hæmochromogen, and hæmine, in the violet and ultra-violet. He observed the following absorptions:—

a. Oxyhæmoglobine.—A defibrinised solution of blood (20 per cent in a stratum of 1 m.m. in depth) absorbed the rays of the wave-lengths λ 465 to λ 358; a solution of 10 per cent absorbed from λ 450 to λ 381. If blood was diluted to 5 per cent the band extended from λ 440 to λ 396. A 1 per cent solution of blood showed in the yellow and the green merely a faint darkening, whilst there appeared a distinct band between λ 427 and λ 405. On further dilution the breadth of the absorption band decreases little; it declines in intensity, and entirely disappears at a dilution of 1 : 600.

b. Hæmoglobine.—For reducing oxyhæmoglobine there was used ammonium sulphide, or a solution of 1 part ferrous sulphate and 1 part tartaric acid in 10 parts of water, to which, shortly before use, 6 parts of "officinal liquid ammonia" are added. (Why does not the author express the strength of his ammonia in some standard universally understood?) Both reduction liquids must be as nearly colourless as possible before use, as they will otherwise darken the violet. A solution of hæmoglobine diluted to 10 per cent is impervious to the rays from λ 450 to λ 398, and one at 5 per cent from λ 447 to λ 408. The absorption in the violet here undergoes, in comparison with oxyhæmoglobine, a displacement towards the less refrangible part of the spectrum. The middle of the absorption band coincides with Frauenhofer's G line, and with a 1 per cent solution the absorption band—sharply defined on both sides—is visible in the violet between λ 437 and λ 417. Hæmoglobine has therefore, in the visible part of the spectrum, not one absorption band, but two bands. In the ultra-violet hæmoglobine is distinguished from oxyhæmoglobine merely by a stronger darkening of the most refrangible rays. A 6 per cent solution is transmissive to about λ 240.

c. Methæmoglobin was generally obtained by adding potassium ferricyanide to a solution of blood. The 10 per cent solution, in which the four absorption bands may still be distinctly recognised in the visible spectrum, absorbs in the violet from λ 440 to λ 358. The band seems washed out towards the ultra-violet on diluting the solution. If mixed with equal parts of distilled water, this solution absorbs from λ 430 to λ 382; if diluted to 1 per cent it allows all the light to pass through without hindrance as far as the violet rays from λ 420 to λ 400. In the ultra-violet, except a darkening of the most refrangible rays, there occurs no independent absorption.

By the addition of a small quantity of ammonia or potassium hydroxide the above-described image characteristic for methæmoglobine (in the so-called acid solution) disappears, and there appears a spectrum similar to that of oxyhæmoglobine, though the first absorption band is split into two.

Besides the two or three bands the author observed, on sufficient concentration, also an absorption band in the green between λ 555 and λ 525, which he has not found already described. The band in the violet in a 10 per cent solution extends beyond H to λ 375, and the side situate towards the red extends to λ 445. If the solution is diluted to 5 per cent only traces of absorption are to be found in the yellow and the green, whilst the space between the Frauenhofer lines G and H is darkened. In a 1 per cent solution the band recedes on one side to λ 415 and on the other to λ 405. In the invisible spectrum the only difference between methæmoglobine in an acid solution and in an alkaline solution is that by the latter the extreme ultra-violet is more strongly darkened.

d. Cyanmethæmoglobine, readily obtained by the addition of hydrocyanic acid to solutions of methæmoglobine, behaves like hæmoglobine; but in a 1 per cent solution, in a stratum of 1 m.m. in depth, absorbs the light rays from λ 580 to λ 523. The darkening of the violet extends beyond H, gradually fading from λ 450 to λ 381. On the addition of hydrocyanic acid the methæmoglobine band in the violet is therefore displaced towards the red. This phenomenon is observed more distinctly in a 1 per cent solution where the chief absorption is situate between λ 430 and λ 410. The photographic image of the ultra-violet shows that the most refrangible rays are absorbed by cyanmethæmoglobine, which increases with the increasing concentration of the solution.

e. Sulphomethæmoglobine, obtained by the action of hydrogen sulphide upon oxyhæmoglobine or hæmoglobine, besides the absorption band in the red, displays a band in the violet, and a darkening in the ultra-violet similar to that of methæmoglobine. A 10 per cent solution absorbs from λ 452 to λ 400: in a 5 per cent solution the limits of the band are seen at λ 440 and λ 408. A 1 per cent solution of blood treated with hydrogen sulphide absorbs from λ 427 to λ 415.

f. Carbon monoxide hæmoglobine likewise displays an absorption in the violet, even at so great a dilution that the bands in the yellow and the green are no longer visible. A 10 per cent solution of carbon monoxide blood shows on the photographic plate an absorption from λ 440 to λ 388. A 5 per cent solution absorbs from λ 430 to λ 407. If the solution contains 1 per cent of carbon monoxide blood the two characteristic bands in the yellow-green disappear, but the band in the violet is seen between λ 425 and λ 411.

g. Hæmatine was obtained by boiling an ammoniacal solution of blood, or one mixed with acetic acid. The absorptive power of acid hæmatine is exceedingly feeble for the violet rays on this side of H. Beyond H, both when the sun or the electric spark is used as a source of light, a very slight darkening, beginning at H and extending to about Cd_{12}.

The alkaline solution of hæmatine, even if much diluted, shows a band, certainly much washed out; its limits for a 10 per cent solution may be fixed between λ 432 and λ 348; a 5 per cent solution displays merely a darkening of the rays between λ 425 and λ 358. Besides an absorption of the extreme ultra-violet rays, there occurs in both cases a faint darkening at Cd_{12} and Cd_{17}.

h. Hæmochromogen is formed on treating solutions o hæmatine with alkaline reductive agents. In the forensic demonstration of blood this substance plays a great part, on account of its uncommonly visible absorption bands; since solutions of blood-spots many years old, whose hæmatine bands would be visible only in the red, and visible only in very concentrated solutions if converted into hæmochromogen, show distinct absorptions in the green even when strongly diluted. Hæmochromogen is the more sharply characterised by its absorption band in the violet, which becomes visible on great dilution, and is therefore still more valuable for a judicial investigation. A solution at 1½ per cent which transmits yellow and green light without hindrance, and consequently does not allow the recognition of the well-known absorption spectrum, still absorbs strongly the rays from λ 430 to λ 418. A 1 per cent solution causes the disappearance of the rays between G and H in the spectrum; a 10 per cent solution absorbs the rays from λ 443 to λ 400.

The most refrangible ultra-violet rays are strongly absorbed by hæmochromogen; a 4 per cent solution is impervious to rays more refrangible than Cd$_{17}$.

i. Hæmin, or hæmatine hydrochlorate, dissolved in methyl alcohol, shows in the violet an absorption band, the middle of which coincides with H. The hæmin solution is perfectly transmissive for ultra-violet light.

According to all the above the absorption band of the blood-pigment, as well as of its derivatives, is more permanent than the already more generally known and repeatedly described absorption bands in the visible part of the spectrum.

Hence it appears the more important that in hæmoglobine, carbon-monoxide hæmoglobine, and hæmochromogen, the absorption band in the violet enters into the visible part of the spectrum, and can be observed by the employment of diffused sunlight as a band defined on both sides. According to the observations of d'Arsonval the violet of the spectrum can be strongly extended towards the ultra-violet if the sun's direct rays or the light of an arc, concentrated by a lens of 10 c.m. in diameter with a very short focus, are allowed to fall into the slit of a spectroscope, and the dazzling rays from red to blue are eliminated by means of a disc of deep blue glass. In this manner of observation prisms and lenses of glass may be used, which is of the greatest importance for practical detection.

In connection with this subject I may mention two remarks of A. Wetzel (*Chemiker Zeit.*, xiv., *Rep.* 87) on the recognition of blood containing carbon monoxide. He shakes gently 10 c.c. of the substance in question with 15 c.c. of a 20 per cent solution of potassium ferrocyanide and 2 c.c. of acetic acid of medium strength (1 vol. glacial acid and 2 vols. water), whereon the blood coagulates to a mass which gradually solidifies. Normal blood yields a black-brown clot, blood containing carbon monoxide a light red. Or we dilute 1 part blood with 4 parts water, add thrice the volume of solution of tannin, and shake round. The difference of colour between normal blood and that containing carbon monoxide increases on standing. After twenty-four hours the normal blood is grey, and that containing carbon monoxide crimson red. The difference is still to be distinguished after ten months. —*Zeitschrift fur Anal. Chem.*, xxxiii., p. 771.

CORRESPONDENCE.

USE OF MINERAL OIL FOR EXCLUDING AIR IN PAVY TITRATIONS.

To the Editor of the Chemical News.

Sir,—I have delayed replying to Professor Brauner's letter published in the Chemical News (vol. lxxi., p. 292) until I had ascertained whether there was any foundation for his suggestion that one of the secretaries of the Chemical Society, "who *alone* are responsible for the abstracts in the *Proceedings*," had taken the astounding course of substituting the name "Allen" for that of "Soxhlet" in the abstract in question.

I am now in a position to inform your readers, upon official authority, that the Secretaries of the Chemical Society are *not* responsible for the above change of name, alleged by Professor Brauner to have been made.

Professor Brauner says that "instead of charging him with dishonest action, I should have sent him a copy of my paper, and given him private information." Unfortunately, at the time when the abstract appeared I was not aware of the existence of Professor Brauner, whom I know simply as the reader of certain papers before the Chemical Society on March 21st. I did all I could to communicate with Professor Brauner. I wrote to the Secretaries of the Chemical Society, informing them that the device had been previously described by me in three different journals, and I added: "The prior publication of the suggestion has evidently been overlooked by Professor Brauner, to whom I shall be obliged if you will forward this letter or communicate its substance." I am informed by the Secretaries that this request was promptly complied with, and have learned later that their letter did not receive any acknowledgment from Professor Brauner, who now states that he did not receive it.

As to the value of the use of mineral oil to exclude air in performing Pavy titrations, it is curious that the device is the only point in the paper communicated by Professor Brauner which the Secretaries of the Chemical Society appear to have considered worth including in the abstract which they prepared.—I am, &c.,

Alfred H. Allen.

Sheffield, July 1, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 24, June 17, 1895.

Professor Newcomb was elected as a Foreign Associate of the Academy, *vice* the late Prof. von Helmholtz. Herr Bachlund was elected a correspondent of the Section of Astronomy, *vice* the late R. Wolff; and Dr. Kowalewski correspondent of the Section of Anatomy and Zoology, *vice* the late M. Cotteau.

Law of Absorption of the Bands of the Spectrum of Oxygen.—J. Jansen.—The law is that the absorbent power of oxygen gas, relatively to these bands, is proportional to the thickness of the gaseous mass multiplied by the square of its density.

Combination of Free Nitrogen with the Elements of Carbon Disulphide.—M. Berthelot.—The author, whilst pursuing his researches on argon, has recognised the direct combination of free nitrogen with the elements of carbon disulphide. This combination takes place by the influence of electricity employed in the form of sparks or of the effluve. When operating on 15 c.c. of nitrogen at normal pressure, the volume having been increased to 25 c.c. by the addition of a small quantity of liquid carbon disulphide, carbon and sulphur are precipitated mixed with condensed carbon subsulphides; at the same time, nitrogen is fixed on the products.

New Combination of Argon: Synthesis and Analysis.—M. Berthelot.—(See p. 1).

Preparation and Properties of Pure Melted Molybdenum.—Henri Moissan.—(See p. 2).

Action of Phenyl Isocyanate upon the Campholic, Carboxyl-campholic, and Phthalic Acids.—A. Haller.

—The compounds obtained are the hydroxycamphocarbonic, iso-, and tere-phthalic acids.

Discovery of a Third Permanent Radiation of the Solar Atmosphere in the Gas of Clèveite.—H. Deslandres.—The permanent radiation of the solar atmosphere, λ 706·55, is emitted by the gas of clèveite, and it even seems to announce a new element common to the solar and terrestrial atmospheres. There is now only a single permanent radiation of the solar atmosphere which has not been recognised on the earth; that is the green ray λ 531·16, called the ray of the corona. It is distinguished as being peculiar to the most elevated regions of the atmosphere, which allows us to suppose that it belongs to a gas lighter than hydrogen.

Molecular Transformations of Chromic Hydrate.—A. Recoura.—The author has previously shown (*Ann. de Chim. et de Physique*, Series 7, vol. iv.) the existence of two varieties of chromium hydroxide, differing from each other by their capacity of saturation for acids. 1. The normal hydroxide is the precipitate produced by alkalis in the solution of a normal salt of chromium. It can fix 6 mols. of hydrochloric acid, evolving 41·4 cal. $= 6 \times 6·9$, and re-generating normal chromium chloride. The chromium hydroxide of the green solution is formed by decomposing by an alkali a solution of a salt of chromium previously rendered green by ebullition. It fixes only 4 mols. of hydrochloric acid. Chromium hydroxide, a hexatomic base, is transformed into a monatomic base, like the alkaline bases, after remaining for three hours in soda. If left for a longer time, it becomes a mixture of monatomic hydrate and of a hydrate of no atomicity.

Certain Basic Haloid Compounds of the Alkaline-Earthy Metals.—M. Tassilly.—The author has prepared and examined the strontium oxybromide and oxyiodide, and the corresponding barium salts.

Action of Heat upon the Double Alkaline Nitriles of the Metals of the Platinum Group: Compounds of Iridium.—A. Joly and E. Leidy.—The study of the double nitriles of iridium and the alkaline metals presents more difficulties than that of the corresponding compounds of ruthenium and rhodium. The double insoluble iridium and potassium salt is not remote from $(IrO)_6O_5(OK)_2$, which would be the potassium salt of a hexairidious acid. On operating at incipient redness in a muffle, the authors obtain a salt approximating to the formula $12IrO_2.K_2O$, the potassium salt of a dodeca-iridious acid.

On the Acid Ammonium Sodium Tungstates.—L. A. Hallopeau.—The author has obtained two salts, $16WO_3,3Na_2O_3(NH_4)_2O+22H_2O$, which loses 15 mols. of water at 100°; and $12WO_3,4Na_2O,(NH_4)_2O+25H_2O$, losing 19 mols. of water.

Rotatory Powers of some Amylic Derivatives in the State of Liquid and of Vapour.—Ph. A. Guye and A. P. do Amaral.—The results of the authors are given in the form of tables.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 111.

New Process for the Purification of a large number of Organic Substances, Alimentary and Otherwise; in particular, Sugars, Alcohols, Potable Waters, &c.—E. Maumené.—The author's invention is the employment of a permanganate (potassium or calcium). The novelty of the process, as far as water is concerned, needs no discussion, since it is admitted in a foot-note that it is used by several London water companies.

Alloys of Iron and Chrome.—R. A. Hadfield.—(*Journal of the Iron and Steel Institute*). Abstracted by R. Masse.

Composition and Constitution of certain Alloys.—C. R. A. Wright.—From the *Journal of the Society of Chemical Industry.*

Progress of the Blast Furnace.—Paul Bayard.—It is here remarked that it is in Germany where the Thomas and Gilchrist process has made the most rapid and the most considerable progress. In 1883 it was under 500,000 tons, and has now reached 2½ millions.

MISCELLANEOUS.

Immunity against the Poison of the Cobra.—According to a paper read before the Royal Society of Edinburgh by Prof. T. R. Fraser, animals—man included—can be made non-susceptible to the venom of the cobra by the injection of minimal doses, gradually increased. He determined firstly the minimum dose fatal to rabbits, and then gradually increased the quantity until he reached an amount fifty times greater than the original fatal limit. A rabbit which he exhibited had thus received, in one hundred and fifty days, cobra poison enough to kill two horses! The effect on the general health of the subject was favourable; it had increased in weight from 2000 grms. to 3000; whilst its strength, and especially its virile power, was signally augmented. A successful antidote for the poison of the cobra is found to be a mixture of $\frac{1}{240}$ c.c. of the serum of a rabbit immunised up to thirty times the minimum fatal dose. We fear, however, that the shrieks of the zoöphilists will render this process useless in the British Empire.

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.

Electric Furnace.—I shall be pleased if any correspondent can supply me with information relating to electric furnaces for laboratory purposes.—Chemist.

THE CHEMICAL NEWS.

Vol. LXXII., No. 1859.

NEW STUDIES ON THE FLUORESCENCE OF ARGON, AND ON ITS COMBINATION WITH THE ELEMENTS OF BENZENE.

By M. BERTHELOT.

I have thought it useful to study in a more thorough manner the conditions of the combination of argon with benzene under the influence of the electric effluve, and those of the special fluorescence which accompanies it.

M. Deslandres, whose special competence in questions of photography is known to the Academy, has kindly lent me his assistance for these new determinations effected by means of stronger dispersions and defined by accurate photographs. It is my duty to express to him my thanks for this prolonged and difficult study.

We must remember that the combination of argon with the elements of benzene under the influence of the effluve is effected slowly; according to the present research it is effected with the co-operation of mercury, which intervenes in the state of a volatile compound. The use of discharges of great frequency does not appear to modify the general characters of the reaction.

At the outset we perceive nothing in diffused light; it is only in the dark room that we perceive a feeble violet light, similar in its intensity to that which the effluve generally develops in gaseous systems. After the lapse of an hour in the dark room we see a green light appearing, which occupies the middle of the interval between the spirals of the band of platinum coiled around the effluve tube; the luminous spectrum presents two yellow rays, 579 and 577 (in wave-lengths), a green ray, 546, and a green band, λ 516·5, These various rays will be defined presently.

The photographic spectrum now taken, with an hour's exposure, shows the principal bands of nitrogen, as well as a blue ray, 436, a violet ray, 405, and an ultra-violet ray, 354; these latter are fainter than the bands of nitrogen.

During the successive hours the green light augments without ceasing, the yellow rays and the ray 546 increase, and the band 516·5 diminishes. After eight hours the bands of nitrogen have almost disappeared in the photographs, doubless because the corresponding nitrogen has been absorbed by the benzene.

Several further hours of effluve bring the fluorescence to a brilliant emerald light, visible in full daylight: the intensity of this phenomenon is not comparable with the fluorescence developed by the effluve in any known gas. The yellow and green rays may be seen and defined by spectroscope in full daylight.

The photographs have shown the rays 579, 577, and 546; 436, 405, 354, 313, and 312 (ultra-violet). We perceive, further, two violet rays, 420 and 416, scarcely visible, and the rays 385 and 358.

The spectrum observed at the end of fifteen hours remained constant during thirty consecutive hours.

Although we have had recourse to photography to register these phenomena, we must not confound such effects observable in full daylight, and at a normal pressure, with the lights developed by the effluve on highly rarefied gases, such as are commonly observed with the spectroscope.

This is the signification of these rays:—

The ray 579 is precisely one of the rays visible in full daylight, and at normal pressure which I have mentioned (*Comptes Rendus*, cxx., p. 800), indicating its probable fission. We must approximate to it the rays 580·1 and 577·1, mentioned in the spectrum of rarefied argon by Mr. Crookes (Jan. 24, 1895). The ray 546 has also been indicated (547) in my former paper, and corresponds to a strong ray, 545·6, exhibited by Mr. Crookes to the spectrum of rarefied argon. M. Deslandres has recognised these same rays in the spectrum of a specimen of rarefied argon which he had prepared by means of lithium. I have verified, by juxtaposition, the coincidence of the latter ray of rarefied argon with that of my effluve-tube. I have also pointed out the ray 436, found in the photograph, and very near to the 434·5 of the rarefied argon by Crookes. The rays 420 and 416 coincide with the very strong rays 420·1—419·8 and 415·96 of the rarefied argon of Crookes. The ray 405 may be identified with the ray 404·4 of Crookes (argon); I have verified the coincidence. The ray 385 coincides with a strong ray 385·15 of Crookes (argon); the ray 354 with a group of 354·7—353·4 of strong rays of rarefied argon (Crookes), and the ray 358 with a group of strong rays 358·7—357·5, observed by Crookes (in argon); λ 516·5 is a band of rarefied hydrocarbides; 313 and 312 are rays of the rarefied vapour of mercury.

None of these rays, as I have already remarked, coincides either with the ray of helium (587·5) or the principal ray of the aurora borealis (557), though this latter falls very near to a strong ray of argon (555.7). If the present fluorescence is not the same as that of the aurora, yet its development and the approximation of the rays above mentioned establish a probable relation between this meteor and the occurrence of argon in the atmosphere.

There appears here a very important circumstance. Already, on examining the table of the rays of rarefied argon given by Mr. Crookes, we recognise that certain of these rays coincide with certain of the rays of the rarefied vapour of mercury. The same coincidence is observed also in the finest rays visible in full daylight, at the normal pressure, in the fluorescence developed during the reaction of benzene upon argon. Such are, according to M. Deslandres, the yellow rays 579 and 577; such is the characteristic green ray 546; such are the blue ray 436, the violet ray 405, and the ultra-violet ray 354. On the contrary, the rays 420, 416, 385, and 358, belong only to argon, and the rays 313 and 312 to mercury.

M. Deslandres attributes the presence of the common rays to the presence of the vapour of mercury either in the rarefied argon or in the fluorescent light obtained with benzine at a normal pressure.

Nevertheless, as no known gas furnishes either this fluorescence or these rays, under the normal pressure, when operating over mercury, it is not possible to explain its formation by the mere presence of this vapour. Otherwise we could not comprehend why they do not equally originate with pure argon in presence of mercury at the normal pressure, and why they are not produced at the first moments of the effluve neither with argon saturated with benzene or carbon disulphide over mercury, nor with nitrogen under the same conditions in which it combines with benzene and carbon disulphide. On the contrary, with argon saturated with benzene they are developed only after the lapse of several hours, and consequently of the progressive transformation of the benzene into one of a series of compounds more and more condensed. It is one of these compounds which, at the moment of its formation, commences to unite simultaneously with argon and mercury, associated possibly in virtue of their common character of monatomic molecules. The fluorescence begins whilst there still exists in the tubes a considerable proportion of liquid benzene; it is then accompanied by a decrease of the gaseous volume.

This fluorescence subsists for a very long time, even after the benzene is no longer perceptible; finally the fluorescence ceases to manifest itself in full daylight, in consequence of the very prolonged action of the effluve, which at length causes the green tint to disappear, and brings back this gaseous system to a luminosity like that of ordinary gases. This happens doubtless in consequence of the total destruction of the last traces of benzene and of the intermediate condensation products, which would maintain the equilibrium of dissociation of the system.

When once the green fluorescence is well established, the compounds which develope it are stable, *per se*; for it suffices, even after twelve hours of rest, without having disarranged the apparatus to cause the effluve to act anew, to re-establish the fluorescence, in all its splendour, in less than a minute. It is, however, extinguished immediately as soon as the electric action is suspended.

But if we separate the gas from the condensed matter, the phenomenon can be no longer reproduced immediately either upon the one or the other. The gas alone, if submitted to the action of the effluve, acquires almost immediately a peculiar violet fluorescence, visible in the dark, and which precedes the development of the beautiful green fluorescence. Still this is not then reproduced, which seems to indicate that the condensed matter may contain one of the products necessary for the equilibrium. If, on the other hand, we re-introduce fresh argon into the tube containing the condensed matter (free from visible benzene) the green fluorescence is not reproduced in its totality, but at the end of some time we see appear near the surface of the mercury, there where the rain of fire is most intense, a localised green tint which presents specific rays, though in a manner not very distinct. Their appearance is due, no doubt, to the existence (or the regeneration) of a trace of benzene, more or less modified. In fact, if we then introduce a few drops of liquid benzene into the tube containing the condensed matter and the fresh argon over the mercury, the action of the effluve for half an hour is sufficient to cause the green tint to re-appear in full splendour. But if there is an excess of benzene the phenomenon requires several hours for its re-appearance.

These various observations, in conjunction with the limited character of the absorption of argon, show the existence of a complex equilibrium in which there intervene at once argon, mercury, and the elements of benzene, or rather a condensed compound derived from them.—*Comptes Rendus*, cxx., p. 1386.

ON ARGON.

By D. MENDELEEFF.

Is argon a chemical individual or a mixture? is it a simple or a complex body? Mendeleeff replies as follows:—The assumption that argon is a mixture appears quite improbable, as is especially shown by the experiments of Olszewski. The assumption of the composite character of argon has also little probability, though its exceptional stability is to a certain extent characteristic of some compounds. If we accept argon as an element, and further assume that its molecular weight is = 40, we must discuss a series of suppositions as to the atomic weight of this substance, which will evidently depend on the number of atoms in the molecule of argon corresponding to the series $A, A_2, A_3, \ldots A_n$. To the first case there would correspond an atomic weight of about 40, when argon would appear as a monatomic element and as an analogue of Cd and Hg. For this view we have the relation K of the specific heats, which for argon has been found = 1·66. We must, however, consider that for the biatomic molecule of chlorine K = 1·3 instead of 1·4. If so active an element as chlorine possesses a smaller K, the extremely inactive argon must have a greater K, although its mol. consists of two or more atoms. For the atomic weight $A = 40$ there is no corresponding place in the periodic system. If the density of argon is below 20, it would come, according to its atomic weight, between chlorine and potassium, and must find its place in the eighth group of the third series; though in this series the existence of the eighth group is scarcely admissible. Hence the assumption of an atomic weight $A = 40$ is scarcely probable.

To the second supposition, A_2, there corresponds an atomic weight = 20, and argon must be introduced into the eighth group of the second series, *i. e.*, immediately after fluorine and before sodium, which is also not too probable, though more so than the case $A = 40$. If we accept A_3, and if its atomic weight is consequently about 14, argon would appear as a condensed nitrogen, N_3. In favour of this view speaks the common existence of argon and nitrogen in Nature; many lines of their spectra fall very near to each other, and the inert character of argon is intelligible if formed from N_2 with liberation of heat, and lastly, its formation from chemical nitrogen. This hypothesis, that $A = N_3$, might be tested by the introduction of boron or titanium into an atmosphere of argon through which electric sparks are caused to strike, and with strong heating.

If we assume A_4 or A_5 the atomic weight of argon would be = 10 or 8, and it would find no place in the periodic system. If we finally accept A_6, and assume 6 atoms in a mol. of argon, there results an atomic weight of about 6·5, and the element falls in the first series, probably in the fifth group.

Hence the two most probable assumptions are:—1. That argon is a polymer of nitrogen = N_3. 2. That the argon molecule is hexatomic, of course admitting that it is a pure elementary substance.

A. Gorbow remarks that the chemical inertness of argon is possibly due to its absolute dryness, since its discoverers have always dried it with P_2O_5. He is of opinion that argon is possibly a nitrogen compound, *e.g.*, nitrogen silicide.—*Russian Physico-Chemical Society*, 1895, pp. 17 to 20, and *Zeit. Anorg. Chemie.*

COMPARISON BETWEEN THE SPECTRA OF THE GAS OF CLEVEITE AND OF THE SOLAR ATMOSPHERE.

By H. DESLANDRES.

The great discovery, by Prof. Ramsay, of a method of obtaining the gas helium, previously recognised only in the sun's atmosphere, equally interests astronomers and chemists.

At the outset the gas of clèveite and the sun's atmosphere have been respectively identified merely by the yellow ray D_3, which they emit strongly; still the last communication from Prof. Clève seems to indicate other common radiations. I have therefore resolved to compare carefully the two lights over the greatest possible extent of the spectrum.

A capillary spectral tube, closed with a plate of quartz, was prepared and arranged so as to receive the gases emitted by a small crystal of clèveite, first heated and then brought in contact with pure rectified sulphuric acid. The spectra of the tube were accurately taken down before heating, after heating, and after the action of the acid, so as to recognise the gases successively liberated and to eliminate alien lights.

Before heating, the spectral tube, the pressure on which was about $\frac{1}{20}$ m.m., showed some of the rays referred to argon; then on heating (to about 300°) there was a plentiful liberation of an oxygen compound of carbon, apparently derived from a dissociated compound; for when the heat was continued the interior pressure increased and diminished on allowing the tube to cool. The yellow ray D_3 appeared only when the sulphuric acid had been in contact with the clèveite, at the same time with other strong rays, luminous and ultra-violet.

The author has collocated in a table the strongest new rays with their intensities (from 1 to 10, 10 signifying the strongest), and, in a parallel column, the rays already indicated by Prof. Clève. He remarks, in a note, that after the ray D_3 he has not detected the rays announced by Mr. Crookes. Opposite the above he has placed the nearest rays of the solar chromosphere, as determined by Mr. Young in the luminous region and by himself in the ultra-violet region. The intensities are represented with a scale of 1 to 100, and another column shows the frequency of these chromospheric rays, *i.e.*, the number of times that they occurred in the atmosphere in 100 observations. The rays which occur always are thus followed by the number 100; they are called *permanent* rays. They are not numerous, as we find only 11 in the luminous region, 5 being due to hydrogen and 2 to calcium. The four others, among which is the ray D_3, are not referred to known elements.

The gas of clèveite emits, therefore, besides the ray D_3, several other strong rays of the chromosphere, and in particular the ray 447·18, which is permanent, so that the number of the sun's permanent rays not recognised upon the earth is reduced to two.

Lastly, other strong rays of clèveite, such as the green ray λ 501·60 and the ultra-violet ray λ 388·8, have in the sun's atmosphere neither the same relative intensity nor the same frequency as the ray D_3; thus we are led to think that the gas is a mixture or a compound.

I will mention two other facts in support of this opinion:—

The ray D_3 in the spectral tube is seen only in the capillary part and at the positive pole; it is wanting at the negative pole, whilst the green ray λ 501 is there very brilliant.

Lastly, Prof. Lockyer has found, in bröggerite, a mineral closely allied to clèveite, only a part of the foregoing rays.—*Comptes Rendus*, cxx., p. 1112.

DETERMINATION OF SULPHUR IN CAST-METAL, IN STEELS, AND IRON.

By LOUIS CAMPREDON.

Principles of the Method.

1. LIBERATION of the sulphur in the form of gaseous compounds, by attacking the metal with dilute hydrochloric and sulphuric acids.

2. Passage of the gases, with the addition of carbonic acid and hydrogen, into a tube of porcelain heated to redness, according to the indications of Rollet to transform the sulphurous compounds disengaged into hydrogen sulphide.

3. Causing the gas to bubble through a slightly acid solution of zinc acetate, to retain the hydrogen sulphide in the state of zinc sulphide insoluble in weak acetic acid.

4. Sulphydrometric titration of the zinc sulphide formed by means of a standard solution of iodine and a solution of sodium thiosulphate, to determine the quantity of iodine present in excess. The end of the reaction is marked by the very distinct disappearance of the blue colour of the solution in presence of starch (added as indicator), when no trace of free iodine remains.

The zinc sulphide formed, submitted to the action of an excess of iodine, gives $ZnS + I = ZnI + S$.

This reaction, the exactitude of which has been verified, is effected in a neutral liquid or in an acid liquid without action upon the zinc sulphide.

Description of the Apparatus.

It includes two continuous appliances for the production of carbonic acid and hydrogen. These gases pass into a solution of silver nitrate, to hold back the sulphuretted compounds which they may contain; they then arrive in the solution flask, where they mix with the gaseous products resulting from the action of the acid employed upon the metal. The gases are cooled by their passage into a condensing flask immersed in water, and which retains the greater part of the watery vapour. The gaseous mixture then traverses a tube of porcelain heated to orange redness or to incipient whiteness, and bubble into a Durand flask containing 100 c.c. of solution of zinc acetate, prepared according to the directions given below. Finally, the gases traverse a solution of lead acetate (slightly acidified with nitric acid), which must not be rendered turbid by the passage of the gaseous current, thus proving that all the hydrogen sulphide has been kept back.

Method of Manipulation.

We operate upon 2, 5, or 10 grs. of the metal, according to its supposed proportion of sulphur.

The apparatus having been fitted up, as shown above (the current of carbonic acid being established and that of hydrogen arrested), we introduce the metal in fine filings into the solution flask, taking all the due proportions to avoid the formation of an explosive mixture, for which purpose it is sufficient to maintain in the tube, at the beginning of the operation, an atmosphere of carbonic acid.

The stopper of the solution flask is inserted, and we introduce, by means of a tube-funnel fitted with a cock, 100 c.c. of sulphuric acid at 1 : 5, or of hydrochloric acid at 1 : 3. The action is kept up in the cold for two or three minutes, still maintaining the stream of carbonic acid; heat is then applied, and the current of hydrogen is allowed to enter.

In the first Durand flask there is formed a white flocculent precipitate of zinc sulphide.

When the reaction is completed we remove the conical solution flask, as also the first Durand flask containing the zinc sulphide. The tubulures are washed by means of a jet from the washing-bottle, to remove any adhering portions of sulphide, and we separate the tubulure. The titration is effected in the Durand flask itself, so as to dispense with any transfer of the precipitate.

We add, from a burette, a known quantity of iodine, more than sufficient to decompose the zinc sulphide according to the equation indicated above; we leave the reagents in contact for two or three minutes, stirring the mixture, and then add 2 c.c. of liquid starch-paste, which produces a greenish colouration. We then run into the flask from a burette, stirring the liquid gently, sodium thiosulphate, until the colouration—which was at first deep green and then indigo-blue—disappears entirely. The iodine acting upon the sodium thiosulphate in presence of water produces sodium tetrathionate and hydriodic acid.

Preparation of the Solutions.

1. *Zinc Acetic Solution.* — Dissolve 10 grms. pure zinc oxide in 25 c.c. of crystallisable acetic acid, dilute to about half a litre, add an excess of ammonia until the precipitate of oxide formed re-dissolves, and then render it slightly acid with acetic acid.

2. *Solution of Iodine.* — Dissolve 7·9 grms. of triply sublimed iodine and 25 grms. potassium iodine in 1 litre of water.

According to the formula of the reaction—

$$\underset{16}{HS} + \underset{127}{I} = HI + S,$$

we see that—

$$\frac{127}{16} = \frac{7{\cdot}9}{1},$$

so that 7·9 grms. of iodine correspond to 1 grm. of sulphur.

3. *Starch Liquor.*—Take 1 grm. of wheat starch, pulverise in a mortar, add a little water to obtain a thin paste, which is poured into a beaker of Bohemian glass containing 150 c.c. of boiling water; let settle, and decant the clear liquid.

Fresh starch liquor ought to be prepared daily.

4. *Solution of Sodium Thiosulphate.*—Dissolve 10 grms. thiosulphate in water, adding 2 grms. ammonium carbonate and water enough to make up 1 litre. The ammonium carbonate increases the stability of the thiosulphate.

The iodine and the thiosulphate solutions are preserved in the dark in bottles of yellow glass.

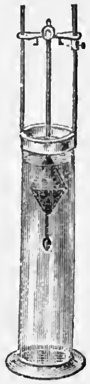
Conclusion.

The process just described is very expeditious; the sulphur is determined in thirty minutes at most. For cast metal the action must be prolonged a little, to make sure that it is complete. This we ascertain by changing the first Durand flask, and substituting a second one containing a clear solution of zinc acetate. If in this second flask there is produced a precipitate of zinc sulphide, it is titrated like the former.—*Comptes Rendus*, cxx., 1051.

ON A NEW FORM OF CHEMICAL BALANCE.

By H. JOSHUA PHILLIPS, F.I.C., F.C.S.

The writer has recently been experimenting with hydrometers, to ascertain to what extent they could be applied to act as a chemical balance; the result of which was, after several trials, the making of an instrument which for certain purposes will be found to be useful. The following is a sketch and description of the instrument:—



It consists of a glass cylinder upon the top of which can be fixed a portable brass ring containing two upright guide-rods of brass, 6 inches high and $\frac{1}{8}$ inch in diameter. The balance proper consists of gilded brass bulbs into which is screwed an aluminium stem. Screwed on to the top of the stem there are arms, also of aluminium, which are perforated at each end so that the guide-rods can pass through them. Upon the centre of the arms there is a receptacle for a small aluminium scoop or pan to hold the substance to be weighed. Underneath the arms it will be seen there are projecting needle-points; there is also a movable point upon one of the guide-rods. The manner of using the instrument is as follows:—The cylinder is first filled with cold recently-boiled water; the bulbs and attachments are then dropped in, the guide-rods passing through the perforations of the arms. The balance sinks into the water until the bulbs are just covered. Supposing 0·2 grm. of steel drillings are desired to be weighed. A 0·2 grm. weight is dropped into the portable pan; the bulbs then sink to a definite depth, and which can be ascertained by bringing the movable needle-point upon the guide-rod so as to face the point fixed upon the arm. The weight is now taken off, and the bulbs rise again. The sample of steel drillings is now gradually introduced into the empty pan until the needle-points are again opposite each other,—gently tapping the instrument to remove any friction,—and the 0·2 grm. of steel is thus quickly obtained. The range of weight that such an instrument is capable of recording must of necessity be of narrow limits. The depth to which the instrument will sink in the liquid with a given weight, and also its delicacy, will depend upon the diameter of the stem. The diameter of the stem of the balance shown in the sketch is $\frac{1}{16}$ inch, and a load of 0·2 grm. will sink it about $3\frac{7}{8}$ inches. The height of the cylinder is 10 inches, and its diameter $1\frac{7}{8}$ inches, and the total length of the stem $5\frac{1}{2}$ inches. An instrument of these dimensions will be found useful for weighing steel for carbon tests, &c., and also for weighing certain precipitates, &c. The sole makers are Messrs. Townson and Mercer, of 89, Bishopsgate Street, London, E.C.

Palace Chambers, Westminster, S.W.

CHEMISTRY OF THE LIGNOCELLULOSES: A NEW TYPE.

By W. C. HANCOCK and O. W. DAHL.

The pith-like stem of *Aeschynomene Aspera** offers a very exceptional instance of wood formation. Although, from considerations of external resemblance, it is often described as a *pith*, its morphological characteristics are those of a true wood (De Bary, "Comparative Anatomy of the Phanerogams," p. 499). The reactions of this wood-substance, on the other hand, show important exceptions from those characteristics of the lignocelluloses. Solutions of aniline salts and of phloroglucol in HCl give the faintest colouration only with the main mass of the cellular tissue, reacting strongly with only a few cells situate near the central axis, and certain vessels disposed at intervals and concentrically in the radial line of cells.

In this preliminary microscopical examination our results were confirmed by competent botanists, who described this wood as consisting in the main of cellulosic tissue, with a small proportion of lignified elements disposed as described.

Having submitted the material to exhaustive chemical investigation on the lines laid down by Cross and Bevan ("Cellulose," p. 94), we find it to be a lignocellulose of normal constitution. Those reactions and decompositions which are related to constitution are identically those of the typical members of the group. But these typical characteristics are associated with divergence in minor points, and particularly in regard to the absence of those constituents upon which the colour-reactions in question depend. It has previously been shown (Cross and Bevan, *Chem. Soc. Trans.*, 1883, p. 18) that the yellow reaction with aniline sulphate is a reaction of an aldehydic or quinonic by-product. Thus the jute-fibre substance, after boiling in a solution of sulphite of soda, or when re-precipitated from solution in $ZnCl_2-Aq$, no longer reacts with aniline salts.

Similarly the phloroglucol reaction is that characteristic of pentosanes, and is no doubt due to their presence in the majority of lignocelluloses. In the particular instance of *Aeschynomene* we have a wood giving the large yield of furfural characteristic of the group, but the pentosan reaction only in scattered cells.

The wood of *Aeschynomene* affords, therefore, another and striking instance of furfural yielding constituents of tissues *not* pentosans (*comp. Ber.*, 1894, 1061).

The following are the results of experimental determinations of the more important reactions and constants.

Physical Characteristics.

The cylindrical stems are made up chiefly of thin-

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* The plant is one of the Leguminosæ, of aquatic habit, the wood being modified to serve as a float. The product has extensive industrial uses, *e.g.*, in the manufacture of pith helmets. See "Dictionary of Economic Products of India," Watt, vi., p. 125.

walled, air-filled cells; 1 grm. of the substance having the enormous volume of 45 to 50 c.c.

The substance in its natural form appears opaque white; on compressing to denser masses it is seen to have a yellowish colour.

Reactions.

With solution of aniline salt a faint yellow, giving the reaction of the lignocelluloses only in isolated cells. With phloroglucol and HCl, a faint pink; the full red colouration characteristic of the lignocelluloses (pentosane constituents) in isolated cells only, as with the preceding reagent.

With Schulze's solution (I in KI + $ZnCl_2$) a brown colouration, giving place to greenish-blue in washing.

With a solution of iodine in strong aqueous hydriodic acid (1·5 sp·gr.) it is stained a pure blue, not removed by washing.

The ordinary woods are stained purple-brown with this reagent, which is changed to brown on washing. In this reaction, therefore, there is a decided resemblance to the celluloses.

With the aniline colours the tissue is dyed in most cases uniformly. So also with ferric ferricyanide (*infra*). In this reaction the tissue shows the distinctive characteristics of the lignocellulose group.

The tissue, unlike the majority of lignocelluloses, does not reduce Fehling's solution on boiling.

Composition.

In the air-dry condition the substance retains only 8·6 per cent moisture. The mineral constituents amount to 1·9 per cent.

Elementary Analysis.—The following results were obtained, calculated in the dry ash-free substance:—

C	46·9	46·2
H	7·1	6·4

These numbers are approximately those of the jute fibre substance.

Alkaline Hydrolysis. — On boiling with alkaline solutions (1 per cent NaOH) the substance rapidly loses 29·0 per cent of its weight. On prolonged boiling (60 minutes) the further action of the alkali is only slight, the total loss of weight being 29·8 per cent.

Cellulose. — After boiling with alkaline solutions as above, and washing, the substance gives with chlorine the ordinary reaction of lignocelluloses, forming a yellow quinone chloride, dissolved by sodium sulphite (sol.) to a deeply coloured solution. The cellulose isolated by this treatment amounted to 54·4 per cent.

Constants of Chlorination.

Determinations were made of the volume of chlorine absorbed in the above reaction, and of the hydrochloric acid formed; the quantities being calculated to the reduced weight of the product, *i. e.*, the weight after boiling with the alkaline solution (Cross and Bevan, *Chem. Soc.*, 55, 199).

(*a.*) Weight of wood, 1·24 grms.; reduced weight, 0·966 grm.
Conditions: Moist Cl gas at 21·5° and 760 m.m.
Time in minutes: 0 5 10 15 20 25 40 50 60 210.
C.c. gas absorbed: 0 44 55 60 64 66 70 72 79 94.
Total absorption calculated to chlorine at 0°, 760 m.m.—84·5 c.c.

(*b.*) Weight of substance, 2·062 grms.; reduced weight, 1·610 grms.
Conditions: Moist Cl gas at 19·5° and 766 m.m.
Time in minutes: 0·5 10 15 20 25 30 35 40 50 60.
C.c. gas absorbed: 0·71 79 86 91 95 97 98 99 102 106.
Total absorption calculated to Cl at 0°, 760 m.m. —93·3 c.c.

The main reaction reaches its limit after about thirty minutes' exposure; the subsequent exposure is due to secondary reactions, attended by decompositions of the chlorinated derivatives.

This conclusion is confirmed by the following determinations:—

	(*a.*)	(*b.*)
Chlorine as HCl formed in the reaction	0·1526 grm.	0·1278 grm.
Chlorine in combination with wood constituents	0·0750	0·1633
Total chlorine	0·2276	0·2911
Total Cl estimated by absorption	0·2782	0·2964

It is evident that the abnormal figures of experiment (*a*) are due to the prolonged exposure of the substance to the halogen.

Taking the figures for the total absorption after thirty minutes' exposure to the gas, when the main reaction may be regarded as completed, they are, calculated on the weight of the lignocellulose taken: in (*a*) 20 per cent, in (*b*) 16 per cent; mean 18·55 per cent.

The combined chlorine estimated in (*b*), also calculated on the lignocellulose, is 10 per cent. This reaction, therefore, is shown to be that generally characteristic of the lignocelluloses; the quantitative results being intermediate between those obtained for the jute fibre, on the one hand, and the woods on the other ("Cellulose," p. 180).

Furfural.

The furfural constants, determined by the method of Flint and Tollens (*Landw. Vers. Stat.*, xlii., 381). The furfural was estimated in the entire wood substance, and also in the products of the alkaline hydrolysis. Results were as follows:—

	Furfural.
Whole wood substance	11·6 p.c.
Products of alkaline hydrolysis, soluble ..	3·6
,, ,, ,, insoluble..	8·0

Of the total furfuroids, therefore, 69 per cent remain in the residue unattacked by the alkaline solution. As the proportion of residue is 70 per cent of the original wood (*supra*), it will be seen that the ratio to the other constituents, or, in short, the distribution of the furfuroids, is unaffected by the alkaline treatment. The furfuroids therefore are not present as pentosanes, or at least are in small proportion.

Methoxyl.

The substance was treated according to the method of Zeisel: OCH_3 estimated = 2·9 per cent, calculated on the dry ash-free substance. This number is considerably less than for the woods generally, and 20 per cent less than for jute. (See Benedikt and Bamberger, *Monatsheft*, ii., 260—267.)

Ferric Ferricyanide Reaction.

The reaction of the lignocelluloses with the solution, obtained by mixing ferric chloride with potassium ferricyanide in equivalent proportions, is a distinguishing characteristic; and the wood of *Aeschynomene* gives an equally pronounced reaction, being dyed evenly to the deepest colour with a very large increase of weight, due to the fixation of the ferroso-ferric cyanide. The following results were obtained:—

(*a.*) 1 grm. lignocellulose increased to 1·958 grms.
(*b.*) 1 ,, ,, ,, 1·747 ,,

the lignocellulose being boiled in water to expel air, and digested some hours with excess of solution of ferric-ferricyanide, obtained by mixing normal solution of Fe_2Cl_6 and $K_3Fe(CN)_6$ in equal volumes. The gain in weight, due to absorption of the blue cyanides, exceeds 100 per cent, calculated on the dry ash-free lignocellulose.

In the resulting products the Fe was determined as

Fe_2O_3 and the N as NH_3, and the molecular ratio Fe : CN found to be 1 : 2·4. The blue cyanide fixed by the lignocellulose has the composition $Fe_5(CN)_{12}$.

Nitrates.

The substance shows the usual reaction of the lignocelluloses with nitric acid in presence of sulphuric acid. It is coloured to a red-brown, which gives place to a bright yellow on washing. It gives low yields of nitrate (110 per cent), and in this respect is shown to be constitutionally more really related to the woods than to the fibrous lignocelluloses. The nitrates, moreover, contain a low proportion of $O.NO_2$ groups, yielding on analysis N = 7—9 per cent—and are insoluble in the usual solvents of these compounds.

Thiocarbonate Reaction (*J. Chem. Soc.*, 1893, 837).

The lignocellulose yields to a certain extent to the joint action of the caustic alkalis and carbon disulphide, the reaction which ensues resembling that of the jute fibre.

The substance is gelatinised, but only a small proportion — 20 to 30 per cent of its weight — passes into solution when treated with water. This affords additional evidence of the small proportion of free alcoholic OH groups.

By the foregoing results this peculiar product of growth is completely identified as a lignocellulose. To botanists this identification will have a special significance as presenting a type of lignification of unique characteristics. Regarded from the chemical point of view, the most important points established and confirmed are:—

1. The existence of a lignocellulose having the essential constitutional features of the group, but devoid of free aldehydic groups and characterised by colour reactions, which are only in part those of the lignocelluloses generally; in others showing a close resemblance to the celluloses.
2. Certain colour reactions, frequently regarded as essentially characteristic of the lignocelluloses proper, are in effect due to by-products.
3. Owing to the unusual conditions of growth, and metabolism obtaining in a tissue, specialised to serve an exceptional function, these by-products are not formed in a large proportion of the cells, which are nevertheless shown to consist of true lignocelluloses.
4. That the true lignocelluloses contain furfural-yielding constituents—furfuroids—which are not pentosans.

Note.—We are indebted to the authorities of the Imperial Institute for a liberal supply of the raw material.

Laboratory of Messrs. Cross and Bevan,
London, W.C.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

First Paper: The Analysis of Strontic Bromide.*

By THEODORE WILLIAM RICHARDS.

Earlier Work.

A glance at published results shows that the atomic weight of strontium has not been investigated for thirty-five years. The early determinations, good enough for their time, show variations which render them quite unsatisfactory to-day; and the case is parallel in every respect to that of barium, which has formed the subject of two recent papers (*Proc. Amer. Acad.*, xxviii., 1; xxix., 55).

The oldest experiments of any note upon the atomic weight of strontium are those of Stromeyer (*Schweig. J.*, xix., 228; Meyer u. K. Seubert's "Atomgewichte," p. 123), who measured, in 1816, the gas evolved from strontic carbonate upon its decomposition by an acid. The result, which is only of interest historically, gives Sr = 87·3, if a litre of carbon dioxide weighs 1·977 grms. under normal conditions.

At about the same time Rose (*Poggendorff's Annalen*, viii., 189) found that 181·25 parts of argentic chloride could be obtained from 100 parts of strontic chloride,—data which indicated Sr = 87·31. Twenty-seven years afterward, in 1843, Salvetat (*Comptes Rendus*, xvii., 318) determined by loss of weight the carbon dioxide in strontic carbonate, and concluded that the metal must be 88·0,—a result which scarcely improved the situation.

Subsequently, in 1845, Pelouze (*Ibid.*, xx., 1047) found the amount of silver necessary to precipitate a weighed amount of ignited strontic chloride; his results give the value Sr = 87·70. Thirteen years later Marignac (*Liebig's Annalen*, cvi., 168) repeated these experiments, determining also the amount of crystal water in crystallised strontic chloride, as well as the amount of strontic sulphate obtainable from the salt. Thus he found that 15·000 grms. of crystallised strontic chloride yielded 8·9164 grms. (corrected by L. Meyer u. K. Seubert, "Atomgewichte," pp. 78, 79) of the anhydrous salt and 10·3282 grms. of strontic sulphate; moreover, 15·000 grms. of hydrated strontic chloride required 12·1515 grms. of silver for precipitation. Another similar series of experiments upon the water of crystallisation made its amount appear 3 m.grms. more than before. These data give basis for a number of possible values for the atomic weight of strontium, ranging from 87·17 to 87·55, the individual figures being tabulated below.

In 1859 Dumas (*Liebig's Annalen*, cxiii., 34) published another determination of the ratio of strontic chloride to silver, the salt having been fused in a stream of hydrochloric acid. Altogether, 27·3435 grms. of strontic chloride required in his hands 37·252 grms. of silver, the individual values for strontium varying from 87·3 to 87·8. Since this time the subject has remained untouched.

Below is tabulated a list of the various determinations, grouped according to the ratios determined.

The Atomic Weight of Strontium.

Oxygen = 16·000.

From the carbonate:—	
Stromeyer, 1816	87·30
Salvetat, 1843	88·00
Ratio of strontic and argentic chlorides:—	
Rose, 1816 ?..	87·31
Ratio of anhydrous strontic chloride to silver:—	
Pelouze, 1845	87·70
Marignac, 1858	87·48
Dumas, 1859	87·53
Ratio of crystallised strontic chloride to silver:—	
Marignac, 1858	87·52
From the crystal water in strontic chloride:—	
Marignac, 1858	87·35
Ratio of anhydrous and crystallised strontic chloride to strontic sulphate:—	
Marignac, 1858	87·2 to 87·6
Selected by Clarke	87·58
Selected by Meyer and Seubert	87·5
Selected by Ostwald*.. ..	87·5

A critical review of the list reveals a great lack of trustworthiness in all the figures. The values deduced from the carbonate, and those involving water of crystallisation, may all be thrown out at once; and the results yielded by the displacement of hydrochloric by sulphuric acid are but little better. The series upon which most

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* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*.

* Much assistance in preparing this list has been obtained from the well-known works of these authors. The figures have all been based upon the most recently accepted atomic weights.

chemists have relied—the one based on the titration of the chloride by means of silver—is hopelessly vitiated by the imperfect execution of the method of analysis (*Proc. Amer. Acad.*, xxix., 80 *et seq.*). If any further proof of this uncertainty were needed, the following table, giving a comparison of the work of different experimenters upon other chlorides, would furnish it:—

Molecular Weight of Chlorides by the Method of Gay-Lussac.

	Pelouze.	Marignac.	Dumas.	Stas. 1st.	Stas. 2nd.
NaCl ..	58·434	—	58·468	58·506	58·503
KCl ..	—	74·539	—	74·583	74·600
NH_4Cl ..	53·464	53·450	—	53·530	53·532

Thus Pelouze, Marignac, and Dumas all obtained low results with the method of Gay-Lussac; in fact, the error sometimes exceeded the tenth of 1 per cent. The cause of this error, which appeared also in the work of these experimenters upon barium, has already been pointed out in another paper (*Proc. Amer. Acad.*, xxxix., 80.).

We are thus led to infer that the true molecular weight of strontic chloride must exceed the usually accepted value, 158·4, by about one-tenth of 1 per cent, and that the true atomic weight of strontium must be nearly 87·7. This inference is confirmed by the result of the investigation now to be described.

The balance and weights, and the methods of weighing and of tabulating results employed in the work recounted below have already been described in sufficient detail (*Proc. Amer. Acad.*, xxvi., 242; also xxviii., 5). The balance seems to have increased slightly in sensitiveness during its four years' work, owing perhaps to the smoothing of microscopic roughnesses in the bearings. It is almost needless to say again that the weights were carefully standardised from time to time, and the small, surprisingly constant corrections were always applied. The correction to the vacuum standard was calculated by the usual formula:—

$$\left(\frac{0{\cdot}001293}{\text{sp. gr. substance}} - 0{\cdot}000156\right)\frac{H}{760}\,\frac{273^\circ}{273^\circ+t^\circ}$$

= correction in grms. for 1 grm. of substance.*

The values thus calculated for the appropriate substances at 20° and 760 m.m., were as follows:—

Correction to be Applied to One Grm. of Substance.

Silver	−0·000031 grm.
Argentic bromide	+0·000043 ,,
Strontic bromide	+0·000141 ,,

The general plan of the following work was similar to that adopted in the case of barium. For obvious reasons the bromide of strontium was chosen as the starting-point; and the investigation began with a study of the properties of the salt, in order to determine its fitness for the purpose.

The atomic weight of silver is assumed to be 107·93, and that of bromine 79·955, unless a definite statement to the contrary is made.

Properties of Strontic Bromide.

The properties of the bromide of strontium resemble very closely those of the corresponding salt of barium. As is well known, however, the strontium salt usually crystallises with six instead of with two molecules of water. The crystals, unlike those of the barium salt, are noticeably hygroscopic in ordinary air, so that they cannot be weighed with great accuracy; they melt easily in their own water of crystallisation at about 100°. This latter fact renders more difficult the quantitative drying of the salts; indeed, in the few cases where the water of crystallisation was determined, it was necessary to allow the crystals slowly to lose their water in a desiccator before ignition. Thus it was found in the following experiment that five molecules of water were given off, the sixth having very little, if any, tension at ordinary temperatures.

	Grms.
Initial weight of strontic bromide	1·3305
Constant weight after three weeks over H_2SO_4	0·9926
Heated to 200° for three hours	0·9246
Loss of weight in dry air, found	=25·41
,, ,, ,, calc. for $5H_2O$	=25·33
Additional loss on ignition, found	= 5·11
,, ,, ,, calc.	= 5·06

A week's standing in the air of the laboratory sufficed to supply again all the water which had been lost. These results point without doubt to the existence of a definite substance having the formula $SrBr_2 . H_2O$, which is hygroscopic in the air and corresponds to the compound $BaBr_2 . H_2O$, obtained in a similar way (*Proc. Am. Acad.*, xxviii., 12, footnote). The existence of this substance has already been inferred by Lescœur (*An. de Chim. et de Phys.* [6], xix., 553, 1890) from observations of the vapour tension of the crystal water. Anhydrous strontic bromide is perhaps even more hygroscopic than the corresponding salt of barium.

Strontic bromide melts to a transparent liquid at 630° (Carnelley), losing bromine in noticeable quantities if exposed to the air for some time at this temperature. Fused in a current of dry hydrobromic acid the salt soon recovers this lost bromine, and upon subsequent solution in water shows itself to be wholly neutral both to phenolphthalein and to methyl orange. It will be seen that this fact is of the utmost significance. The cold fused transparent or translucent mass is much less hygroscopic than the powder from which it was made.

The importance of driving out every trace of water from the salt before weighing cannot be over-estimated. Systematic experiments (*Proc. Amer. Acad.*, xxviii., 12; xxix., 58) with baric bromide and chloride led to the conclusion that probably neither of these salts retains water at a red-heat, and it was to be expected that the same fact might be true of the substance in hand. In order to test the point, 4 grms. of very pure strontic bromide dried at about 400° were fused in a stream of hydrogen bromide. The mass *gained* nearly 6 m.grms. in weight, showing that the loss of bromine in the air at 400° much more than counterbalanced a possible trace of water. Again, 11·2610 grms. of the same specimen, dried at 305° until constant in weight, were found to weigh 11·2630 grms. after fusion as before. Since these gains corresponded closely with losses of bromine found alkalimetrically in similarly heated but unfused samples, it is evident that very little if any water can be held by the dried salt. It has already been pointed out that no absolute proof of such a fact is possible (*Proc. Amer. Acad.* xxviii., 14); and these experiments, together with the analogy furnished by the more manageable barium salts, seem to be the last resort. The apparatus used for these experiments will be described under the heading "Method of Analysis."

The specific gravity of anhydrous strontic bromide has been found by Bödeker to be 3·96. Since no more recent data regarding this constant could be found, another determination, described below, seemed to be needed. 3·2560 grms. of a pure specimen which had been fused in the air and dried at 200° in the pycnometer were found to displace 0·6678 grm. of toluol at 24°. Since the specific gravity of the toluol under these conditions, referred to water at 4°, was found to be 0·8618, that of the strontic bromide referred to the same standard must be 4·203. Again, 2·3065 grms. of strontic bromide which had been used in a stream of hydrobromic acid displaced 0·4699 grm. of toluol, thus having a specific gravity of 4·229.

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* H = atmospheric pressure; t° = atmospheric temperature at the time of weighing; 0·000156 = standard weight of air displaced by 1 grm. of brass.

The mean of these determinations, 4·216, was adopted as the basis of the reduction of the weighings to the vacuum standard.

Strontic bromide, like baric bromide and chloride, may be evaporated to apparent dryness over a free flame in a platinum dish without losing a trace of halogen. Experiment showed that, upon mixing pure bromide of strontium with small quantities of bromide of calcium and barium and crystallising the mixture, both impurities tended toward the mother liquors. Hence simple crystallisation affords a method of eliminating the two most likely impurities.

The other properties of strontic bromide do not pertain especially to the present work.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 28th, 1895.

Dr. Gladstone, Vice-President, in the Chair.

Mr. Bowden read a note on "*An Electro-Magnetic Effect.*"

A long glass tube containing mercury, and fitted with a small stand-pipe to indicate the hydrostatic pressure, is passed between the poles of an electro-magnet. On passing a current of about 30 ampères through the mercurt in this tube, the stand-pipe being turned so as to indicate the pressure either perpendicular or parallel to the lines of force of the field of the electro-magnet, movements of the mercury in the stand-pipe take place. When the stand-pipe is perpendicular to the lines of force of the field, the mercury rises or falls according to the direction of the current. When the stand-pipe, however, is parallel to the lines of force, the mercury always *rises* whatever the direction of the current.

Prof. S. P. Thompson said there appeared to be three unexplained effects—one proportional to the current and the field, and reversible; another, independent of the direction of the current or of the field; and a third, which only occurred while the current was changing in strength. In addition there may be a fourth effect, which up to now has not been noticed. The motion of the mercury column in Fig. 1 was in the opposite direction to that of the drag on a conductor carrying the current. An apparent rise in pressure might be due to a decrease in the density of the mercury due to the heat developed by the current.

Mr. Blakesley asked if the author had noticed any changes in level in the mercury reservoirs at the ends of the tube.

The author, in his reply, said the reservoirs at the ends were so large that no changes of level were appreciable.

Mr. Rhodes read a paper on "*The Armature Reaction on a Single Phase Alternating Current Machine.*"

In this paper the author gives the investigations that were the subject of a verbal addendum to a paper read before the Society on a previous occasion. He investigates the lag or lead of the E.M.F.'s over the current, and applies the results to examine whether the field excitation of the generator or the motor is strengthened or weakened by the reaction of the armature currents.

Mr. Tunzelmann expressed a hope that the author would amplify parts of his paper.

Mr. Blakesley said the conclusion of the author, that "either of two alternate current machines may be driven as a motor by the other, irrespective of their relative E.M.F.'s," is not invariably correct. The facts of the case were these:—The E.M.F. of the motor may exceed that of the other machine to a certain extent; but that E.M.F. multiplied by the cosine of the angle of electric lag must yield a product not greater than the E.M.F. of the generator,—*i. e.*, using Mr. Rhodes's symbols, $e \cos \theta$ must not be greater than E. Mr. Blakesley gave a geometrical proof of this; but the same proposition had been given by him some ten years ago, in the course of investigating the subject generally. This was at a time when Dr. John Hopkinson was, with less than his usual perspicuity, teaching that synchronous alternate current machines could not be run in series with stability, both doing work. Referring to the author's diagrams, Mr. Blakesley said that in a problem involving so many elements as that under consideration, it was impossible, with the limited dimensions of space, to represent the results with the complete generality of a formula. Some elements had to be taken as the independent, others as the dependent, variables. The author had considered the power transmitted to the motor, the E.M.F. of the generator, and the angle of electric lag, as independent; the E.M.F. of the motor as dependent. In Mr. Blakesley's original diagrams the E.M.F.'s were both considered independent, as well as the electric lag, and the powers applied or transmitted as dependent variables. In any case the formulæ properly derived from such diagrams became perfectly general, and it did not appear to him that the change of method indicated could properly be called a new theory on the subject. As a matter of fact, diagrams based on the independence of the E.M.F.'s and the electric lag would furnish a better means of discussing the question of the stability of the motion than Mr. Rhodes's plan, and this might account for the entire omission from the paper of this important matter.

Prof. S. P. Thompson said it was impossible to discuss the question of stability till the subject of armature reaction had been thoroughly investigated. The terms lag and lead had been used by Mr. Rhodes in a constant manner; but this was not always done, and he recommended that the phase of the current which was common to both generator and motor be taken as the standard.

The author, in his reply, said he agreed with Mr. Blakesley that there was a limit to the extent to which the motor might be excited, and this upper limit could easily be obtained from the figure given in the paper. The question of armature reaction was, however, most important, as it might excite the field two or three times more than the original excitation. Since motors were designed to do a certain amount of work, and not the work to fit the motor, it was most natural to take the output of the motor as fixed.

Mr. Shelford Bidwell read a paper on "*The Electrical Properties of Selenium.*"

The author has continued his investigations on this subject, and has come to the following conclusions:—(1). The conductivity of crystalline Se appears to depend principally on the impurities which it contains in the form of metallic selenides. It may be that the selenides conduct electrolytically, and that the influence of light in increasing the conductivity is to be attributed to its property of facilitating the combination of Se with metals in contact with it. (2). A Se cell having platinum electrodes and made with Se to which about 3 per cent of cuprous selenide has been added, is, even though unannealed, greatly superior both in conductivity and sensitiveness to a similar cell made with ordinary Se and annealed for several hours. (3). Red Se in contact with copper or brass is quickly darkened by the action of light, owing, it is suggested, to the formation of a selenide. (4). Crystalline Se is porous, and absorbs moisture from the air, and it is this moisture that causes the polarisation of Se after the passage of a current. (5). The presence of moisture is not essential to sensitiveness, but appears to be in a slight degree favourable to it. (6). If cuprous selenide is made the kathode in an electrolytic cell, and a strip of platinum the anode in water, red Se mixed with detached particles of the selenide is deposited in the water. (7). The photo-electric currents sometimes set up when light falls upon Se are dependent upon the presence of moisture, and are no doubt of voltaic origin. (8). Perfectly dry Se is below platinum in the thermo-electric series.

Prof. Minchin (communicated) suggested that the selenium "cell," should be called a selenium "resistance." A grid having one terminal made of aluminium and the other of copper might form a true cell, and might generate an E.M.F. when light fell on it. He (Prof. Minchin) would like to know if the author had tried any such cell in which light, simply and solely, generated an E.M.F. He could not agree that chemical action must necessarily follow the action of light in a cell. For take the case of the oldest photo-electric cell,—the thermopile,—what chemical action can we show here for all the energy of the incident heat? Chemical action due to light may or may not occur, according to the nature of the cell.

Mr. Appleyard asked whether the author had submitted these selenium resistances to the action of electric oscillations. Prof. Minchin's "impulsion" cells were greatly influenced by electric oscillations. The great variation in the resistance with time of the author's cells pointed rather to an effect of contact between the selenium and the electrodes than to an elementary change in the structure or composition. He (Mr. Appleyard) had recently tried to crystallise a supersaturated solution of sodium sulphate by electric oscillations, as well as by direct sparks, and by currents of several ampères; but no crystals could be induced to form. Change of contact rather than change of structure appeared to him to be the most promising direction in which to look for an adequate theory of selenium resistances.

Prof. Ramsay said the quantity of Se liberated in the electrolytic experiment was much too great to be accounted for by oxygen dissolved in the water. The study of Se was very interesting, for this substance was on the border-land between those bodies in which the electric conduction was metallic and those in which it was known to be electrolytic.

The author, in his reply, said he agreed that the name "selenium cell" was not an appropriate one. He had not tried the effect of electric oscillations.

The Society then adjourned till the autumn.

NOTICES OF BOOKS.

The Century Science Series. John Dalton and the Rise of Modern Chemistry. By Sir Henry E. Roscoe, D.C.L., LL.D., F.R.S. London, Paris, and Melbourne: Cassell and Co., Ltd. 1895.

The position of Dalton in the history of science is now so fully established and so universally conceded that it requires no discussion, especially as his career has been already described by W. C. Henry, R. A. Smith, H. Lonsdale, J. Harland, C. Wheeler, and F. Espinasse.

The author pronounces Dalton to be the "founder of modern chemistry," and Joule to be the "founder of modern physics."

But it is strange that these two illustrious *savants* are pronounced to be "Manchester's two greatest sons," to be the "great twin brethren of Manchester," while all the time Dalton was born in the remote Cumberland village of Eaglesfield, and did not become a dweller in Manchester until the age of twenty-seven. Hence, whatever may be said concerning Joule, Dalton was certainly not one who "arose in the midst of a population given up to industrial pursuits, . . . and where most men's thoughts are engrossed in what shallow minds often look upon as common trade avocations." We must here note with regret the political and semi-political remarks introduced, the more gratuitously since Dalton was not a politician, but seems to have wisely felt that the position of the philosopher, as of the poet, "should be higher than on the battlements of party."

It is interesting to find that Dalton, in his pre-Manchester days—if we may coin such an expression, in addition to meteorology, gave some attention to botany and entomology, and his collections remained for some time in the Keswick Museum.

After arriving in Manchester, Dalton published an English grammar, which soon disappeared from circulation. But a Sheffield man re-published it some years afterwards as his own.

Dalton seems to have predicted, before the earliest experiments of Faraday in that direction, that the gases would ultimately be condensed by low temperature and strong pressure.

A chapter is devoted to his remarkable optical defect of colour-blindness, to which he drew attention in a memoir. By a singular piece of bad taste, not a few Continental authorities thought fit to call this defect "Daltonism."

The investigations which led to the "atomic theory" were entered upon early in the present century. In a lecture delivered in January, 1810, he expressed the opinion that the elements are periodical and absolute:—"I should apprehend," he writes, "that there are a considerable number of what may properly be called *elementary* principles which can never be metamorphosed one into another by any power we can control." Still he holds that "we ought to avail ourselves of every means to reduce the number of bodies or principles of this appearance as much as possible."

An account is given of the reception of the atomic theory by other chemists and of the attitude of Dalton towards the theories of others, such as Gay-Lussac and Avogadro. This attitude was generally unfavourable. He would not admit that there are the same number of particles of a gas in a given volume and under a given pressure.

The remaining chapters contain much interesting matter. We learn that, being once unwell, "his doctor ordered a dose of James' powder. Next day the patient was better, and the doctor attributed the result to his prescription. 'I do not well see how that can be,' said Dalton, 'for I kept the powder until I could have an opportunity of analysing it.'" Though not a total abstainer, he seems to have come practically to the same opinion as von Helmholtz, who found that the slightest quantity of alcohol drove away any chance of his "arriving at any new and good scientific idea."

It is recorded that he was the first to introduce the process of volumetric analysis. He became a Fellow of the Royal Society in 1822, and received the first Royal Medal in 1826. It almost sets one's teeth on edge to learn that when Dalton was presented at Court, King William the Fourth could think of nothing more appropriate to say than:—"Well, Dr. Dalton, how are you getting on at Manchester—all quiet, I suppose?"

Notwithstanding the existence of other memoirs of Dalton, this little work deserves warm recommendation.

A Treatise on Practical Chemistry and Qualitative Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By Frank Clowes, D.Sc., Professor of Chemistry at the University College, Nottingham; Member of the Councils of the Institute of Chemistry and of the Society of Chemical Industry; Fellow of the Chemical Societies of London and Berlin. Sixth Edition. Crown 8vo., pp. 469. London: J. and A. Churchill. 1895.

This work holds a convenient intermediate position between the bald epitomes which are now so common and the elaborate works of Fresenius, Rose, &c. Having already passed through the ordeal of six editions, it may be considered as in harmony with general requirements.

It has the advantages that the rarer elements are not ignored, special tables being furnished for their recognition. Instructions are given for the detection of organic acids, alkaloids, and other organic substances. The use of the blowpipe, the microscope, and the spectroscope is kept in view. The student is recommended to buy pure reagents, rather than to attempt their preparation, which will in general involve a great outlay of time.

In nomenclature little need be said. Glucinum has, we believe, the claim of priority, as against beryllium, used by the author. "Mercuria acid" must, however, we submit, be merely a compositor's error.

The illustrations of apparatus and of laboratory arrangements are excellent, as are also the accompanying remarks on manipulation.

Theoretical explanations are very properly relegated to works on descriptive chemistry. The work, in short, merits almost unqualified recommendation, though we may regret the homage paid to the Chinese system in the preface.

The Law of Copyright in Designs; together with the Practice relating to the Proceedings in the Courts and in the Patent Office, and a full Appendix of Statutes, Rules, and Forms, the International Convention, &c. By Lewis Edmunds, D.Sc., LL.B., F.C.S., and F.G.S., Barrister-at-Law; assisted by T. M. Stevens, B.C.L., and Marcus W. Slade, B.A., Barristers-at-Law. London: Sweet and Maxwell. Manchester: Meredith, Ray, and Littler. Dublin: Hodges, Figgis, and Co.; and Ponsonby. Melbourne and Sydney: C. F. Maxwell. 1895. 8vo., pp. 291.

The registration of designs is a method for securing a proprietary right, complementary to patents for inventions. The number of designs registered annually is here stated as about 20,000. It appears that, after several tentative enactments, copyright for three years was granted to any new and original design, whether such design be applicable to the ornamenting of any article or for the shape or configuration thereof, and however it is produced or applied. The classes of manufacture are articles of metal, wood, glass, earthenware, paper-hangings, carpets, shawls, tissues, &c. In 1883 the previous Acts were repealed, and the provisions of the Patents, Designs, and Trade-marks Acts substituted. The decisions under these Acts have been few, and it is admitted that many ambiguities still remain.

The question is raised, What is a design? Then arises the question of novelty.

Next follows publication, which may be effected in a variety of ways. We come then to the question of proprietorship. There are, it seems, five classes of persons who may be considered proprietors: the author of the design; any person who employed the author to execute the work for good and valuable consideration; any person acquiring the design for such consideration; a person acquiring the right to apply the design to articles; and, lastly, persons on whom the design on these rights may devolve.

There is an elaborate section on infringement and the remedies.

In Part II. is given the text of the Patents, Designs, and Trade-mark Acts from 1883 to 1888, so far as they relate to designs, followed by the designs rules of 1890 and 1893, and the details of the International Convention for the Protection of Industrial Property.

The Appendices include the Statutes concerned; the forms; instructions to persons wishing to register designs; and Orders in Council applying the provisions of the Patents, &c., Acts, to British Possessions and Foreign States.

Lastly, follows a bibliography of the literature of copyright in designs.

The book, though of less interest to the majority of our readers than the authors' companion volume on Patents for Inventions, will prove highly valuable to counsel and solicitors, and more especially to patent agents.

The Prospector's Handbook. A Guide for the Prospector and Traveller in Search of Metal-bearing or other Valuable Minerals. By J. W. Anderson, M.A., F.R.G.S., F.I.Inst., Author of "Fiji and New Caledonia." Sixth Edition, thoroughly Revised and much Enlarged. Fcp. 8vo., pp. 176. London: Crosby Lockwood and Son. 1895.

This handy little book ought to be the pocket-companion of every frontier-man and explorer of the Far South. It will, we believe, guard the prospector against two opposite evils, viz., collecting and carrying away matter of no value and overlooking precious deposits. Both these mistakes have been very often made; yellow micas and certain pyrites have been taken for gold, and, on the other hand, platinum, nickel, and cobalt have been tossed aside as worthless. The author's advice is the more valuable because he is not a mere compiler, reproducing the work of others in different language, but a field-geologist, who has gained experience in New Zealand, New Caledonia, Mexico, and the Western States of America.

A valuable feature of this little book is, that it makes a minimum demand upon the scientific or technical knowledge of the prospector, as well as upon his funds and upon his means of conveying apparatus. Processes which are excellent in a fixed laboratory are worthless if they require the use of heavy and delicate instruments. The use of the blowpipe is very justly recommended. But we would suggest that a pocket spectroscope and a good lens will occasionally prove useful without making an objectionable addition to the traveller's *impedimenta.*

We are glad to notice that, among the substances to be sought for, coal and petroleum are not disregarded.

Vanadium has been overlooked; but it is perhaps more likely to occur among furnace-products, &c., than in native rocks. Nor do we find any mention of potash. Our present commercial supply of this requisite, so necessary alike to the chemical manufacturer and the farmer, is confined to Germany. Hence we suggest that it should be earnestly sought for in the Dominion, Australia, and Africa.

An excellent feature of the work consists in the practical hints which are scattered through it, and which will often direct the prospector to search in right places.

Another useful feature is the glossary of terms used in different countries by miners, metallurgists, &c.

But there is the less reason for us to enlarge on the striking merits of Mr. Anderson's work as it has already reached its sixth edition.

Year-Book of Electro-chemistry. ("Jahrbuch der Elektro chemie.") *Reports on the Advances of the Year* 1894 The scientific part elaborated by W. Nernst, Professor in Ordinary at the University of Göttingen, Director of the Institute for Physical Chemistry and Electro-chemistry. The technical part elaborated by Dr. W. Borchers, Teacher at the Duisburg Royal School for Machinery and Foundries. Vol. I. 8vo., pp. 274. Halle: W. Knapp. 1895.

This work affords a useful summary of the progress effected in electro-chemistry during the year 1894. Prof. W. Nernst first expounds the general scientific points of view which are now accepted.

We find a notice of the researches of Kohlrausch and Heydweiller on the conductivity of pure water. It had been previously shown by the former that water becomes less conductive the more carefully it is purified. It is now proved that finally a limit is reached, or, in other words, that water has a specific conductivity.

In the second part of the work Dr. Borchers discusses the applications of electro-chemistry. He begins with an account of the production of electric energy from chemical energy.

Prof. Ostwald, in a brilliant discourse delivered before the Congress of German Electro-technicists (*Zeit. Elektrotech. und Electrochemie*, 1894, Parts 3 and 4), expressed himself to this effect:—"The way in which may be solved the greatest of all technical questions, the production of cheap energy, must be discovered by electro-chemistry. If we have a galvanic element which furnishes directly electric energy from carbon and the oxygen of the atmoshere, in a quantity fairly proportionate to the theoretical value, we have a technical revolution in comparison with which the invention of the steam-engine must vanish. Only conceive what will be the aspect of our industrial places in view of the incomparably convenient and flexible distribution of which electricity is susceptible. No smoke, no soot, no boilers, no engines, even no fire, since fire will be needed only for the few processes which cannot be conducted electrically." Every chemist will hope that this ultimate prospect is not too fascinating to be realised.

In discussing electrolytic depositions and separations the author quotes (*Zeit. Elektrotech. und Electrochem.*, 1894, 6 and 9, and *Chem. Zeit.*, 1894, Nos. 59 and 71) the complete worthlessness of Rüdorf's directions concerning the current to be applied. The author is of opinion that the prolonged action of Meidinger elements, as recommended by Rüdorf, is not sufficiently constant. He recommends the use of illuminating currents as used for electro-chemical analysis in the laboratory of the High School at Stockholm. Few laboratories possess the motive power for dynamos, and still fewer are not deterred by the expense and the inconvenience of accumulators.

Concerning Hermite's "so-called disinfecting and sanitary processes,"—treatment of sewage,—the most trustworthy accounts are not favourable.

In the application of electrolysis to dyeing there is no novelty of value to be mentioned, the patented processes of Skuzeck and Zelen having been long previously anticipated by Goppelsröder.

No one can doubt that we are, to say the least, on the threshold of surprising modifications and improvements which will be due to the applications of electricity in the chemical arts.

City and Guilds of London Institute for the Advancement of Technical Education. Report to the Governors, March, 1895. Gresham College, Basinghall St., E.C. 1895.

Most of our readers will already be acquainted with the general constitution of the City and Guilds of London Institute, and with the movement of which it is at once the seat and the embodiment. We have here a list of the Governors, including the *ex-officio* members of this body, the Presidents of the Royal and the Chemical Societies, of the Council of the Society of Arts, and of the Institution of Civil Engineers. The President of the Institute of Chemistry is not here included. Then follow the representatives of the Corporation and of those Guilds who are taking part in the promotion of technical education, *i.e.*, the Mercers', Grocers', Fishmongers', Goldsmiths', Merchant Taylors', Salters', Ironmongers', Vintners', Clothworkers', Dyers', Leather-sellers', Pewterers', Cutlers', Armourers' and Braziers', Saddlers', Carpenters', Cordwainers', Plumbers', Coopers', and Plasterers' Companies. In these lists figure among others the honoured names of Mr. G. Matthey, F.R.S., Sir F. Abel, F.R.S., Sir J. D. Hooker, F.R.S., &c. Next follows the Council, comprising most of the above, and the Executive Committee.

The Staff of the Institute's Colleges includes, in pure chemistry, Prof. H. E. Armstrong, F.R.S.; and H. A. Miers, M.A., as instructor in crystallography, besides assistants and a demonstrator. The Staff for applied chemistry comprises Prof. Raphael Meldola, F.R.S., &c., with two demonstrators and a lecture assistant.

We notice certain very encouraging features. Unlike the majority of British schools, the Institution gives as its "results," not the names of pupils who have "passed" some examination, but of former students who have proved, and are still proving in after life, the soundness of the training they have received. Among these sixteen former students in the chemical department receive prominent mention. Chemistry is, however, by no means a favourite subject. Thus of the 186 ordinary students for the Session 1893-94 only 20 are studying chemistry, as compared with 71 engaged in engineering and 95 in physics.

The total number of students attending the day-classes shows a falling-off as compared with the previous session, when the number was 213. Of the day-students, 197 in number, 70 had been previously educated at grammar and other endowed schools; at middle class schools, 69; at private schools, 48; and at public elementary schools, *i.e.*, board and church schools, only 10. Of the 992 evening students attending the College, 39 were engaged by day in the chemical industries. This number is small, but we must remember that these industries occupy in London only a relatively small number of persons.

A glance at the sums presented and subscribed in support of the Institution by the City Companies might be a wholesome lesson for some persons who are in the habit of telling their ignorant hearers that the Guilds expend their resources in riotous living, and that their funds ought to be confiscated for the promotion of fads. It appears that the total amount contributed by these much-slandered bodies, and some of their leading members, has been £453,435 19s. 6d. Of this total £78,964 have been contributed by the Goldsmiths, £68,250 by the Clothworkers, and £66,550 by the Fishmongers. These figures do not include the sums contributed by, *e.g.*, the Clothworkers' Company, towards the technical departments of the Yorkshire College. We find, to our great satisfaction, that the Salters' Company have placed at the disposal of the Institute a sum of £150 yearly, to be applied to founding one or more Fellowships, to be entitled the Salters' Company's Research Fellowships, for the encouragement of higher research in manufacturing chemistry. The first award under this scheme was made in January last, to Martin O. Forster, Ph.D., F.C.S. Dr. Forster had been a chemical student at the Finsbury Technical College during the Sessions 1888—91, and has subsequently graduated at the University of Würzburg.

Mr. F. H. Carr is now a Salters' Company's Research Fellow, in the Research Laboratory of the Pharmaceutical Society.

But though satisfactory progress is being made, we must not, as a nation, forget the immense ground we have to recover, and the energy and means which we have wasted over the cram and the examinational systems.

How much good might be effected if the friends of scientific instruction had at their disposal the large sums which are still being squandered by the various "anti" movements, and in the promotion of valueless fads. The City and Guilds of London Institute is, we are happy to say, not a cramming school.

CORRESPONDENCE.

MYSTERIOUS DISAPPEARANCE OF PECTOSE.

To the Editor of the Chemical News.

Sir,—Would some of your readers kindly inform me why have pectose, pectosic acid, and all the other pectose bodies, disappeared from all modern works on organic chemistry, except the last edition of "Watts' Dictionary of Chemistry"? Had they ever any existence except in text-books, or were they mere mixtures of gums and sugars?—I am, &c.,

Carbo-Hydrate.

USE OF MINERAL OIL FOR EXCLUDING AIR IN PAVY TITRATIONS.

To the Editor of the Chemical News.

Sir,—In my letter on the above subject (Chemical News, lxxii., p. 11) there is an erratum of a rather important nature. Instead of saying that "at the time when the abstract appeared I was not aware of the *existence* of Professor Brauner," what I actually wrote was that "I was not aware of the *residence* of Professor Brauner."—I am, &c.,

Alfred H. Allen.

Sheffield, July 6, 1895.

BRAZILIAN MONAZITE.

To the Editor of the Chemical News.

Sir,—My attention has just been called to an article in the Chemical News (vol. lxxi., p. 181) entitled "North Carolina Monazite," by H. B. C. Nitze. In it he remarks that monazite is found in paying quantities in Brazil.

May I venture to ask that gentleman, through your columns, if he knows in which State of Brazil that mineral is found? If so, would he have any objection to furnishing me with the information?—I am, &c.,

J. Macdonald Kyle.

The Laboratory,
Usina Wigg, Miquel Burnier,
Minas Geraes, Brazil, June 12, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Zeitschrift fur Analytische Chemie.
Vol. xxxiii., Part 5.

Crystalline Hard Combinations in Cementation Steel, and in Alloys of Iron with Chromium, Tungsten, and Manganese.—H. Behrens and A. R. von Linge.—This article commences with an account of the microscopic examination of the metals in question, viz., of crude cement steel, obtained from puddled Dannemara iron; of ferro-tungsten and tungsten-steel; of ferro-chrome, chrome-steel. Then follows an account of the analysis of the metals, qualitative and quantitative.

Sensitiveness of some Zone Reactions, and their Application in the Recognition of Acids.—Hein. Trey.—If the more frequently occurring inorganic acids, including oxalic acid, are grouped in such whose silver compounds are precipitated from acid solutions, such as hydrochloric, hydrobromic, and hydriodic acid, iodic acid, hydrocyanic, hydroferrocyanic, ferricyanic, sulphocyanic, and hydrosulphuric acid; and, further, in such whose silver salts are only deposited in neutral solutions, such as phosphoric, arsenic, arsenious, chromic, oxalic, boric, sulphurous, thiosulphuric, and silicic acids. If we, secondly, divide the acids precipitable by barium, or calcium chloride again into such whose barium salts are precipitated from hydrochloric solutions, *i.e.*, sulphuric and selenic, and hydrofluosilicic acid; and into such whose barium or calcium salts are sparingly soluble in acetic acid, *i.e.*, oxalic, chromic, and hydrofluoric, their detection may be more easily and simply effected as follows:—If the alkaline solution obtained by boiling in sodium carbonate, the original substance—supposed to be soluble in water or other acids—and if silver nitrate is then added in excess, the first mentioned silver compounds of the acids insoluble in nitric acids are precipitated. If we then filter, and add to the filtrate ammonia in such a manner as to superstratify the solution, so that the ammonia, which is specifically lighter, remains floating in the upper part of the test-tube, there appears at the surface of contact of the two liquids a neutral zone, in which place, in presence of the above-mentioned silver salts of the acids precipitable only in a neutral solution, either as a precipitate or as a slight turbidity. If, in the same manner, we add to another part of the alkaline solution hydrochloric acid until the reaction is acid, and then barium chloride, the precipitate formed shows the presence of the above-named acids, which precipitate as barium salts from a hydrochloric solution. If we now add to the filtrate calcium chloride, in order to obtain any oxalic acid or hydrofluoric acid as calcium salts, which are much less soluble than their barium compounds, and if we convert the solution into an acetic liquid by the addition of sodium acetate, we obtain the precipitates of the barium or calcium compounds of the above-named acids, *i.e.*, barium chromate, calcium oxalate, and barium or calcium fluoride. If we set aside those of the acids previously enumerated which have already been detected in searching for the bases, or in dissolving or acidifying the original substance, such as sulphurous acid, thiosulphuric acid, iodic acid, and hydrogen sulphide, the presence of which, moreover, is not possible in an acid solution; if we boil, after the addition of nitric or hydrochloric acid, the proposed method for detecting the groups of acid in question may be given thus:—

Acids Precipitable by Silver Nitrate.

From nitric solution.	From neutral solution.
Hydrochloric acid.	Phosphoric acid.
Hydrobromic acid.	Arsenic acid.
Hydriodic acid.	Arsenious acid.
Hydrocyanic acid.	Chromic acid.
Hydroferrocyanic acid.	Oxalic acid.
Hydroferricyanic acid.	Silicic acid.
Hydrosulphocyanic acid.	Boric acid.

Acids Precipitated by Barium Chloride.

From a hydrochloric solution.
Sulphuric acid.
Selenic acid.
Hydrosilicofluoric acid.

Acids Precipitated by Barium and Calcium Chloride.

From an acetic solution.
Chromic acid.
Oxalic acid.
Hydrofluoric acid.

If the liquid is boiled after the addition of nitric acid (boiling is to be recommended after the addition of silver nitrate, in order to obtain a clear filtrate more easily and quickly), the solution must be allowed to cool before adding the ammonia, as on superstratifying the hot filtrate with ammonia at the ordinary temperature the lower current will stream into the upper, and thus render the superstratify an illusion. This method is satisfactory and easy, only the students are supplied with binormal solutions; that is, such as contain per litre double the equivalent—expressed in grms.—of acid alkali, or salt.

Detection of Iodine in Urine.—Dr. A. Jolles.—The author has obtained satisfactory results by the two following methods indicated by Sandland (*Archiv der Pharmacie*):—1. Precipitating with silver nitrate the specimens acidulated with silver nitrate, reducing the precipitate with zinc and hydrochloric acid, distilling the solution obtained with ferric chloride, receiving the distillate in solution of potassium iodide, and titrating with centi-sodium thiosulphate solution. 2. Evaporating the urine in a platinum capsule on the water-bath after the addition of sodium carbonate, charring and incinerating the residue, slightly acidulating the aqueous solution with dilute hydrochloric acid, and distilling with ferric chloride.

On Oils.—G. de Negri and G. Fabris (translated from the original Italian by Dr. Holde).

Recognition of small quantities of Metallic Sulphides in Precipitated Sulphur.—R. Fresenius.

Determination of the Specific Gravity of Liquids.—C. R. Alder Wright.—From the *Journal of the Society of Chemical Industry*.

Determination of the Specific Gravity of Solids.—H. B. Fulton.—From the *Journal of the Society of Chemical Industry*.

Apparatus for the Direct Determination of the Weight and Volume of Gases.—Krupp and Co. (German Patent 69913 and *Chemiker Zeitung*).—The state of tension of a volume of gas enclosed in a vessel is transmitted to index-works in the manner of an aneroïd barometer to a scale which shows any change of volume or weight. The scale is graduated so that the expansion of the volume can be read off in $\frac{1}{100}$ of the unit of volume at 0° and 760 m.m. pressure.

Melting-point of Cocaine Hydrochlorate, and on the Determination of Melting-points in general.—O. Hesse (*Liebig's Annalen*). — The author finds the melting-point of cocaine hydrochlorate 185—186°, in opposition to Kinzel, who gives it at 200—202°. The difference lies in the execution of the experiment. Kinzel employed the ordinary sulphuric acid bath, whilst Hesse uses Roth's apparatus, in which both the substance and the mercurial receptacle of the thermometer are in air.

Calibration of Pipettes.—Frank Clowes.—*Journal of the Society of Chemical Industry.*

New Photometer.—E. W. Lehmann ("Inaugural Dissertation" and *Annalen der Physik und Chemie*, N.S., xlix., 672).—This apparatus cannot well be described intelligibly without the aid of a diagram or a model.

Some Laboratory Arrangements.—E. B. Voorhees and L. A. Voorhees.—From the *Journal of Analytical and Applied Chemistry.*

Prevention of Rupture of Tubes Melted into Vessels.—C. Ullmann.—The author introduces a known quantity of ether, benzene, or other suitable liquid into a Mannesmann tube, and thrusts the filled tube, closed at the lamp, into the steel tube, which is then screwed up and heated as usual. Thin glass tubes of inferior quality can thus be heated without rupture. Jannasch (*Zeit. Anorg. Chemie*) has used this method with success in opening up silicates with hydrochloric acid. (German Patent No. 68536 and *Zeit. Angew. Chemie*, 1893, p. 274).

Production of Gases for Use in the Laboratory.—L. L. de Coninck (*Chemiker Zeitung*, xvii., 1009).—This paper requires the accompanying figure. A modification of the above-mentioned apparatus has been devised by Franz Meyer (*Chemiker Zeitung*, xvii., 1242).

Syphon of a New Construction.—R. Ebert (*Chemiker Zeitung*).—The long limb of an ordinary suction syphon is fitted into the perforated stopper of a wide boiling tube, the side tube of which can be closed by means of a flexible tube and a pinch-cock. The side tube is fitted into the upper aperture of a parting-funnel. In order to set the apparatus in action the lateral tube is sucked until the main syphon-tube is completely full. The pinch-cock is then closed, and the liquid can be drawn off at pleasure by opening the cock of the funnel. For drawing off fuming acids, ammonia, or other corrosive liquids, the author attaches the lateral tube to a flask fitted with a cock and previously exhausted. On opening the cock, the reduced pressure effects the required suction. A filtration through asbestos or glass-wool can be easily effected by placing a pledget of such substances in the lower part of the funnel. The apparatus may also serve for filtering through paper. In this case, instead of the boiling-tube and parting funnel, the author uses a rather wide glass tube provided with a lateral piece and closed below with a glass cock. Syphons depending on a similar principle have been devised by M. Rücker and by C. Franke (*Zeit. des Allgemein. Oesterreich. Apotheker-Vereins*, xlvii., pp. 54 and 55).

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st inst., Sir James Crichton-Browne presiding. The following were elected Members:—Messrs. Sidney Crompton, Walter Daniel Cronin, A. F. M. Spalding; Lady Evans, and Miss S. Rose-Innes.

Appointments.—Professor Dr. Th. Curtius has been appointed to the chair of chemistry at the University of Tubingen, *vice* the late Lothar von Meyer. Dr. Nanson has been nominated a correspondent of the Paris Academy of Sciences in place of Prof. von Nordenskiold, who has been elected a Foreign Associate.

Testimonial.—On July 1st the students of the Central School of Chemistry and Pharmacy presented Dr. A. B. Griffiths (Lecturer on Chemistry and Physics) with one of Browning's new direct-vision spectroscopes, on the case of which is a silver plate bearing the following inscription:—"Presented to Dr. A. B. Griffiths as a token of esteem and respect by students of the Central School of Chemistry and Pharmacy, July, 1895." It may be stated that this is an addition to Dr. Griffiths's valuable collection of philosophical instruments.

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.

Electric Furnace.—In reply to "Chemist," Messrs. H. N. Warren and Co., Chemical and Electrical Experts, 18, Albion Street, Everton, Liverpool, are manufacturers and inventors of electrical furnaces for laboratory purposes.

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Telegrams, "Firebrick," Leeds.

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July 12, 1895.

THE CHEMICAL NEWS.
Vol. LXXII., No. 1860.

HELIUM.

By WILLIAM HUGGINS, F.R.S.

With the advantage of a bluer sky than I had during my former observations, I saw the fainter component of D_3 to-day. In the chromosphere, close to the limb, both lines are usually expanded, so that the interval between them is very small, and on that account less easy to see. At a little distance from the limb, and especially in suitable prominences, the lines become thin, when the fainter component is easily overpowered if there is much scattered light from haze or thin cloud. D_3 was seen double both near the limb and in a prominence.

I hear that Professor Hale has already seen the solar line double in the United States.

90, Upper Tulse Hill, S.W.,
July 10, 1895.

THE ANALYTICAL CHARACTERS OF A MIXTURE OF SALTS OF BARIUM, STRONTIUM, AND CALCIUM.

By H. BAUBIGNY.

In the determination of the elements present in a saline solution, the detection of the three alkaline earthy metals, barium, strontium, and calcium, is often regarded as delicate. The fact is due merely to the defective character of the methods employed, or to a want of precision in the procedures indicated.

Let us suppose that all the metals precipitable by ammonium sulphide are eliminated, operating in presence of sal-ammoniac to favour their separation. In the liquid we transform, as usual, the three alkaline earthy metals into insoluble carbonates by means of ammonium carbonate. We filter and wash with a dilute hot solution of ammonium chloride. The filtrate will then contain merely the alkaline metals, and magnesium if present.

The mixture of the three insoluble carbonates is re-dissolved with hydrochloric acid, which is added slowly and drop by drop, so as to have a liquid which is neutral, or approximately so. A small excess of acid may be corrected, if needful, by the addition of a proportionate quantity of an alkaline acetate. Under these conditions potassium dichromate precipitates merely the barium, and indeed *all the barium*, the chromate of which is insoluble in free chromic acid or in very dilute acetic acid. We cannot, in a neutral medium, operate with the yellow alkaline chromate, which precipitates equally the salts of strontium, and even those of calcium if concentrated.

We then recognise the strontium by adding to the filtrate a solution of potassium sulphate containing 2·5 grms. of the salt per litre, and in the sole case of the presence of strontium there is a precipitate after agitating for a few seconds.

The concentration of the solution of alkaline sulphate is such, in fact, that the calcium sulphate which might be formed is in presence of a quantity of water more than sufficient to keep it in solution. If there is only calcium present there is the less trouble; moreover, the use of the alkaline sulphate, substituted for that of calcium sulphate, has the advantage of permitting the search for calcium in the same liquid. The strontium sulphate thus obtained has always a yellowish cast, due to a little strontium chromate carried down, in spite of the solubility of this latter salt in the conditions of the process.

To detect the calcium it is necessary to eliminate the chromic acid, as it would vitiate all the remaining operations. To this end, in the filtrate from the strontium sulphate we precipitate in heat the calcium and the residue of the strontium by means of potassium carbonate; we re-dissolve the carbonate, little by little, with hydrochloric acid, correcting the excess of acid, if requisite, with ammonium acetate. To the solution we add a large excess of sal-ammoniac, either in crystals or in a concentrated solution, and a few drops of potassium ferrocyanide.

There is formed at first a turbidity, then a precipitate, which increases rapidly, and which, according to Rose, is a double compound of potassium and calcium ferrocyanide, sparingly soluble in water, and insoluble in ammonium chloride. The sensitiveness is such that a solution of calcium sulphate, with the addition of three to four times its volume of water saturated with sal-ammoniac, is rendered strongly turbid, and precipitated after being stirred up for a minute with a little potassium ferrocyanide.

The salts of strontium produce nothing similar even in a highly concentrated solution; the liquid remains perfectly clear. Still we cannot think of employing this method for the separation of the two metals, since strontium is always carried down, and even if the calcium is in decided excess the totality of the strontium is found in the precipitate.

Barium gives with ferrocyanide the same reaction as calcium, although the sensitiveness is much less even with the use of sal-ammoniac. It is therefore preferable, for greater accuracy, to separate firstly the barium.

These facts having been explained, it is easy to understand the necesssty of removing chromic acid after the separation of the barium, in order to detect calcium in presence of strontium. Free chromic acid oxidises ferrocyanide to the state of ferricyanide, and finally there remains merely neutral alkaline chromate, which occasions the formation of insoluble strontium chromate, whilst at the same time there is produced double potassium and calcium ferrocyanide by the slightest excess of ferrocyanide, the ferricyanide having no action, and thus every conclusion is wanting in the desirable accuracy.

In the case where the existence of calcium is the only question of interest, we heat at first with a concentrated solution of alkaline sulphate; the filtrate then contains sufficient calcium to permit of its detection by ferrocyanide.

This remark leads to a variation in the method indicated for the detection of the three alkaline earthy metals. After having recognised barium by potassium bichromate, and then strontium in the filtrate by the standard solution of potassium sulphate (2·5 grms. per litre), we precipitate the rest of the strontium with a concentrated solution of the same sulphate, filter, saturate the liquid with ammonium chloride, and add ferrocyanide in excess to destroy the free chromic acid. As strontium then no longer exists it cannot form a chromate, and consequently if there is a precipitate it is exclusively due to calcium by the action of the ferrocyanide.

The solubility of the carbonates of these metals in ammonium chloride has been an objection to the precipitation of the earthy alkaline metals by ammonium carbonate in presence of a large excess of sal-ammoniac. If this fact is important in a quantitative respect, there is no reason to exaggerate this importance in ordinary qualitative determinations. In fact, a solution of calcium chloride at 1 part in 1000, and containing 50 per cent of the sal-ammoniac which it can dissolve—that is to say, half saturated—certainly gives only a scarcely perceptible turbidity with ammonium carbonate; but if we add ammonia to destroy the bicarbonate which always exists, and apply heat, there is produced a very appreciable action. It is the same with barium and strontium.

Even when reduced to these slight proportions the qualitative analysis is not always defective. Still experience has taught me that in these limits it is advantageous to modify the process a little. Let us suppose that the liquor charged with sal-ammoniac contains quantities of barium, strontium, and calcium, only in the proportions of thousandths of the weight of that of the solvent. Under such conditions neutral chromate precipitates neither lime nor strontia. If this reagent gives a precipitate it is because barium is present. After stirring and waiting for a few moments we filter. All the barium having been separated, we treat with a drop of sulphuric acid; if strontium is present, a precipitate of sulphate is quickly formed.

Lastly, in another portion of the liquid, which must be saturated with ammonium chloride, we try the reaction with potassium ferrocyanide; a solution of barium (1 part in 1000) giving nothing, whilst with calcium, even at a strength considerably inferior, we have still a very decided opalescence.

Another difficulty in presence of a great excess of sal-ammoniac, if we have a solution very rich in magnesium, is, that on the addition of ammonium carbonate and ammonia, there may occur a separation of the double ammonium and magnesium carbonate. But it is very easy to obviate this inconvenience by diluting the liquid or re-dissolving the precipitate and then adding a hot and dilute solution of ammonium chloride, which re-dissolves the double carbonate. Hence I recommend the precipitate to be washed with hot water slightly charged with sal-ammoniac. Let us add, *e.g.*, to 5 c.c. of a solution of ammonium chloride saturated in the cold, 3 to 5 c.c. of a solution of magnesium chloride (at 1 part in 10); then a little ammonium carbonate and ammonia; the liquid becomes turbid, and in heat the precipitate increases, whilst it disappears if we double the volume by the addition of water. If we have employed only 1 c.c. of magnesium chloride (the proportions of the other substances remaining the same), the precipitate formed in the cold, on the contrary, disappears in part without the addition of water, and the liquid then remains perfectly clear. The proportion of magnesium has, therefore, its importance.

In conclusion, I must point out that no method for the separation of strontium and calcium can be founded upon the simultaneous use of potassium oxalate and carbonate, so that the strontium would be converted into carbonate and the calcium into oxalate, and, after washing, separating by the aid of acetic acid, in which calcium oxalate is distinctly insoluble.

The action in the cold varies, in fact, with the proportions of the two alkaline salts employed. For an excess of oxalate (3 parts to 1 of carbonate), we have only oxalates; for an excess of carbonate (3 parts to 1 of oxalate), almost all the calcium is in the state of carbonate, and the action does not seem more distinct with a mixture of equal parts.

At a boiling heat, in all cases, even if there is a decided excess of oxalate, the action of the alkaline carbonate always predominates both for calcium and strontium.—*Bulletin de la Soc. Chim. de Paris.*

ON AN EXPLOSION: AS A WARNING.

By EUG. BAMBERGER.

My assistants have since last summer prepared the crystalline *p*-nitrodiazobenzene nitrate dozens of times, pressing the substance energetically on the clay plate and rubbing it with the horn spatula without the slightest explosive phenomenon having ever been perceptible. The salt is extremely less explosive than the ordinary diazobenzene nitrate. Whilst a very small quantity of the latter detonates loudly if heated, an equally small quantity of the nitro-derivative deflagrates only with a relatively feeble report. We have frequently rubbed up the salt upon porous earthen plates in quantities of 30 to 40 grms. without any precaution.

Unfortunately a fearful explosion has lately occurred which seems scarcely to be reconciled with previous experience, and the causes of which are not explained with certainty. F. Goose had prepared about 20 grms. of the salt by the direction of my private assistant, Dr. Meimberg, and was gently turning the crystals over on a smooth earthen plate with a glazed porcelain spatula, which had no sharp corners or edges, when suddenly there ensued an explosion with a fearful noise and the most destructive effect. F. Goose lost eight fingers—some entirely and others partially. The sight of his left eye has suffered severely. He cautiously, as he had to do with a diazo-salt, avoided all pressure or rubbing. Since this misfortune we have repeatedly rubbed the nitrate with the porcelain spatula upon clay without any explosion.

F. Goose remembers distinctly that his preparation contained some black sandy grains, which he had chiefly, though not entirely, picked out, and which—as he believes—were derived from the snow used for refrigeration.

Dr. Meimberg has, in fact, been able to produce an explosion by a prolonged grinding up of the salt with remnants of gritty snow. It is merely remarkable that F. Goose should encounter this misfortune on gently and loosely turning it over.

By this opportunity I should wish to give a warning against paranitroisodiazobenzene hydrate. This substance has recently exploded, although nothing of the sort was apprehended, as it was being laid in a pulverised and dried state upon a card paper for the purpose of weighing. There ensued merely a deflagration with a dull report; still it will always be advisable, when working with this substance, to protect the eyes.—*Berichte*, xxviii., No. 6.

A METHOD FOR THE VOLUMETRIC ESTIMATION OF THE PHOSPHORIC ACID, SOLUBLE IN WATER, PRESENT IN SUPERPHOSPHATES.*

By W. KELMAN and K. MEISSELS.

On titrating a solution of phosphoric acid with some normal soda and methyl-orange as an indicator, the final reaction occurs as soon as the salt NaH_2PO_4 is formed,—that is, when one-third of the acid is saturated. If we use phenolphthalein as the indicator, the red colour appears on the formation of the salt Na_2HPO_4. In the acidimetric titration of a solution of acid calcium phosphate, which has a neutral reaction with methyl-orange, there occurs the following transposition:—

$$3CaH_4(PO_4)_2+8NaOH=Ca_3(PO_4)_2+4Na_2HPO_4+8H_2O,$$

when the calcium phosphate is eliminated; 8 mols. NaOH here, therefore, behave as equivalent to 3 mols. P_2O_5. On titrating superphosphates with the assumption of the above transposition, we sometimes, however, obtain differences which show that the various salts present in the superphosphates behave differently to the lime salts, and that a calculation according to the above equation is not valid.

This difficulty can be overcome on the basis of the following consideration:—If we titrate a solution containing acid calcium phosphate, with phenolphthalein as the indicator, and assume, according to the rule of saturation, that 1 mol. NaOH saturates ½ mol. P_2O_5, we obtain on titration too high results; but if, after obtaining the final reaction with phenolphthalein, we filter the liquid off from the precipitate, add methyl-orange, and titrate back with acid, the results of this

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[*] Communication of the Technol. Museum of Vienna, 1894 (*Zeit. fur Anal. Chemie*, xxxiii., p. 764.

titration will be as much too low as those of the former operation were too high. The arithmetical mean of both titrations will give the correct result.

On the basis of these considerations the authors proceed as follows:—20 grms. superphosphate are dissolved, *secundum artem*, to 1 litre. (*a*.) 100 c.c. of the filtrate are mixed with methyl-orange, and exactly neutralised with some normal lye. Phenolphthalein is then added to the same solution, and semi-normal lye is added until the change of colour and the quantity required are accurately noted. This titration requires great attention, since the precipitate during its formation interferes with the recognition of the final reaction. (*b*.) Further, 100 c.c. of the solution of superphosphate are mixed in a 250 c.c flask with a sufficient excess of semi-normal lye, filled up to the mark, shaken up, and filtered. 100 c.c. of this filtrate are mixed with phenolphthalein, neutralised with semi-normal acid, methyl-orange is added, and the liquid is exactly titrated with semi-normal acid. The number of c.c. used must be multiplied by 2·5, in order to obtain the quantity representing 100 c.c. solution of superphosphate.

The arithmetical mean of (*a*) and (*b*) multiplied by 0·0355 gives the grms. of P_2O_5 in 100 c.c. of solution of superphosphate = 2 grms. of the substance.

SIMPLIFIED METHOD FOR DETERMINING PHOSPHORIC ACID BY MEANS OF MOLYBDENUM SOLUTIONS.

By Dr. J. HANAMANN.

As the molybdic method permits the most accurate determination of phosphoric acid in phosphoric liquids, and serves as a check-method for all other determinations of phosphoric acid, but has merely the defect of a double precipitation and of the tedious conversion of the molybdenum precipitate into magnesium pyrophosphate, the efforts of analysts have for some time been directed to its simplification and its conversion into a volumetric form. But the gravimetric determination of phosphoric acid is at present so generally demanded that we have been compelled in case of superphosphates to adopt, in place of the molybdic method, the citrate method, which requires one precipitation only, though in certain phosphoric liquids rich in lime it gives values in excess.

The yellow phospho-molybdic compound has hitherto not been esteemed of constant composition, because, on heating the phosphoric precipitates, molybdic acid in excess is added to the subsiding precipitate, and is thrown down conjointly. We have either to precipitate a part of the molybdic acid by previous repeated boilings from a molybdic solution obtained on Sonnenschein's method, and then effect the precipitation of the phosphatic solution in heat, with the molybdic solution overcharged with nitric acid,—or we must make use of such a molybdic solution as deposits, in the cold and after prolonged agitation of the mixed liquids, all the phosphoric acid of the solution as a molybdic precipitate of a constant composition.

In fact, it is practicable to throw down in the cold, and after vigorous stirring for thirty minutes at common temperatures, from a solution containing to 100 grms. molybdic acid, 1 litre of 10 per cent ammonia, and 1½ litres of nitric acid at 1·246 sp. gr., as also from the Maercker solution after the addition of ammonia. This is effected in such a manner that the precipitate, washed with ammonium nitrate and nitric acid and dried, and gently ignited, has a pure black-blue colour, a constant composition, and contains—in 100 parts by weight—4·018 phosphoric acid. The differences in weight of the precipitate at the various changes of colour from yellow to black are as follows:—

	Grms.
Orange	35·2325
Greenish	35·2140
Black, blue, greenish in the middle	35·2050
Uniform black-blue..	35·2010
Tare	33·9520
	1·2490

Twenty-five c.c. of the solution of sodium phosphate used, treated with the above-named molybdic solution in the manner described, gave a black-blue precipitate weighing 1·245 grms., which, multiplied by 0·04018, $0{\cdot}050 = 184 \times 2$, therefore in 50 c.c. $= 0{\cdot}10036$ phosphoric acid; 50 of this solution contained 0·1 grm. phosphoric acid. By this method we may examine high-class superphosphates, and such as contain iron. as well as arable soils.

The recent smooth dense filters of the firms Dreverhoff, and Schleicher and Schüll, permit of a very complete removal of the precipitate from the filter, and the separate treatment of each, the filter being well incinerated. If the precipitate has not the correct black-blue colour after a slight ignition, it is moistened with a little ammonia, dried, and again ignited. Organic matter is destroyed by previous ebullition in nitric acid or chromic acid. The molybdic precipitate is heated in a platinum crucible, preferably on platinum wire-gauze. The bottom of the crucible must not become red-hot, though the wire-gauze should display redness. At the same time this method of working allows the use of very small quantities of the average liquids. 20 grms. superphosphate were dissolved in 1 litre of water, and 10 c.c. of the solution were poured into 35 c.c. of the molybdic liquid, stirred for half an hour, and filtered cold; the precipitate washed, dried, heated, and weighed. It weighed:—

No. I.—0·9182 grm.
No. II.—0·9180 grm.
$0{\cdot}9182 \times 4{\cdot}018 = 3{\cdot}6893276 \times 5 = 18{\cdot}446$ p.c. P_2O_5.
$0{\cdot}9180 \times 4{\cdot}018 = 3{\cdot}6885240 \times 5 = 18{\cdot}442$ „

After converting the molybdic precipitate into magnesium pyrophosphate, and ignition according to the usual method of Fresenius, there were obtained:—

No. III.—
$0{\cdot}05763 \times 0{\cdot}64 = 0{\cdot}0368832 \times 500 = 18{\cdot}4416$ p.c. P_2O_5.

Twenty grms. of an arable soil, in which there had been obtained gravimetrically, according to the most trustworthy method, 0·140 per cent phosphoric acid, gave by the cold method, when treated with 10 per cent cold nitric acid, after elimination of silica, and calculated on 100 c.c. of the acid solution, ($0{\cdot}7009 \times 0{\cdot}04018$, in which therefore $0{\cdot}028162$ $P_2O_5 \times 5$) in 100 grms. of fine earth 0·14082 per cent P_2O_5.—*Chemiker Zeitung*, vol. xix., No. 25.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

First Paper: The Analysis of Strontic Bromide.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 20).

Preparation of Materials.

Strontic Bromide.—Six different specimens of the salt were analysed, in order to establish the presence or absence of accidental impurities.

In the first place, 500 grms. of the purest strontic nitrate of commerce were dissolved in 2 litres of pure water, and four times in succession a cubic centimetre of pure sulphuric acid diluted with much water was added

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* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*.

to the solution. Each time only a small amount of precipitate appeared at once, the rest appearing slowly. After waiting in each case three or four days, the clear liquid was decanted. No barium could be found even in the first precipitate of strontic sulphate; but it is true that the spectroscope is not a very satisfactory means for the detection of barium under these circumstances. The acid solution of strontic nitrate, which had been thus almost if not quite freed from a possible trace of barium, was evaporated to small bulk, filtered from the precipitated strontic sulphate, and twice successively brought to crystallisation. Each mass of crystals was washed three times with alcohol upon the filter-pump, to free it from the mother-liquor, which might contain calcium or magnesium. After having been converted into pure carbonate by precipitation with ammonic carbonate and long-continued washing, the strontium was combined with bromine. For this purpose hydrobromic acid remaining from the barium work, obtained by repeated fractional distillation of the common acid, was used.

The strontic bromide was evaporated in a platinum dish. This was slightly attacked, bromine having been set free by a little occluded strontic nitrate in the carbonate. After evaporation to dryness the bromide was fused at a bright red heat in platinum. The alkaline solution of the fused cake was treated with hydric sulphide, filtered, acidified with hydrobromic acid, warmed, filtered from the platinic sulphide, boiled to free it from sulphuretted hydrogen, again filtered, and crystallised twice from water. The crystals were washed with alcohol, and the strontic bromide thus obtained is numbered I. below; it was used for the three preliminary experiments, as well as for Analysis 13.

The second sample of strontic bromide was prepared from similarly treated strontic nitrate which had been recrystallised four times instead of twice. The nitrate was converted into oxide by ignition in a nickel crucible; and the dissolved residue was filtered to get rid of a small amount of nickel. Ammonic sulphydrate gave no trace of colouration to a portion of the filtrate. Two re-crystallisations in a platinum bottle sufficed to free the strontic hydrate from a trace of undecomposed oxides of nitrogen, and the last crystals dissolved to form an absolutely clear solution in pure hydrobromic acid (see *Proc. Amer. Acad.*, xxviii., 17, bottom of page). The solution of strontic bromide was evaporated to crystallisation, the crystals were dehydrated, and the anhydrous salt was fused; finally, after solution, standing, and filtration, a fresh crop of crystals was obtained. This sample, labelled No. II., was used for Analysis 14.

Among several different methods for obtaining pure strontic salts, that recommended by Barthe and Falières (*Journ. Chem. Soc.*, Abs., 1892, p. 1277; *Bull. Soc. Chim.*, [3], vii., 104) seemed to promise well, and accordingly the third preparation was based upon their work. The so-called "pure" strontic chloride of commerce was dissolved in water, treated with ammonic hydrate and a little carbonate, and filtered from the precipitate containing iron, aluminium, and so forth. To the filtrate was added an excess of sulphuric acid, and the precipitated strontic sulphate was thoroughly washed with dilute sulphuric acid and then with pure water, in the hope of freeing it from magnesium and calcium. When the wash water became neutral to methyl-orange the precipitate was treated with enough ammonic carbonate solution to convert about half of it into carbonate, and the mixed precipitate was then washed with water by decantation until only a very small constant trace of sulphuric acid (due to strontic sulphate) was found in the decantate. The carbonate was then decomposed by pure hydrochloric acid, and the solution was allowed to stand in a glass flask for nine months over the undecomposed sulphate, with occasional shaking. The strontic chloride was decanted, the sulphate was washed once with water, and the filtered decanted liquid was evaporated in a platinum dish until most of the free hydrochloric acid had been expelled. The dissolved residue was neutralised with ammonia, shaken with a little ammonic carbonate, and then filtered. To the greatly diluted filtrate was added an excess of pure ammonic carbonate, and the precipitate was washed until the wash-water was free from chlorine. The strontic carbonate was dissolved in nitric acid which had been twice distilled in platinum, and the nitrate was crystallised twice successively in a platinum dish. Each quantity of crystals was washed with small quantities of water and three or four additions of alcohol. The first mother-liquor, upon being fractionally precipitated by means of alcohol, showed distinct traces of calcium in the extreme solution; thus Barthe and Falières's method was not capable of freeing the substance wholly from calcium. The second mother-liquor showed no trace of calcium upon the most careful scrutiny.

200 grms. of the purest crystals, after having been dried at 130°, were dissolved in about a litre of the purest water and filtered into a large platinum dish, into which was passed first pure ammonia gas and then pure carbon dioxide through a platinum tube (see "Ammonic Carbonate"). The pure strontic carbonate was washed by decantation eight or ten times, dried on the steam-bath, and ignited in a double platinum crucible over a spirit-lamp.

Part of this carbonate was converted into bromide by means of the purest hydrobromic acid (prepared from pure baric bromide and re-distilled many times; see *Proc. Amer. Acad.*, xxviii., 17), and the product was digested for a long time with a considerable excess of carbonate. After filtration and evaporation the strontic bromide was fused in a platinum dish over the spirit-lamp; the salt being perfectly clear while liquid. The translucent cake was dissolved, allowed to stand, filtered, faintly acidified with hydrobromic acid, and crystallised twice from water. Each time the crystals were washed with the purest alcohol. The resulting bromide of strontium was used for Analyses 1, 2, 3, 5, 6, 7, 12, 15, 16, 17, and 18.

The next sample was prepared from the strontic carbonate which had been digested with the strontic bromide just described. It was dissolved in the purest hydrobromic acid, and purified much as before, except that the salt was fused twice with intermediate crystallisations, instead of only once. This fourth preparation was used for Analysis 9.

The fifth sample was made by the repeated crystallisation of the combined mother-liquors obtained from the four previous preparations. It was used for Analyses 4, 8, and 19.

The sixth preparation of strontic bromide was made from the strontic sulphate remaining from the third. This residue was treated with enough ammonic carbonate to convert all but about 20 grms. of the sulphate into carbonate. The washed strontic carbonate having been dissolved in a slight excess of hydrochloric acid, the residual sulphate was allowed to remain in the solution for a week. After filtration, evaporation to dryness in platinum, solution, a second filtration, treatment with a little ammonic hydrate and carbonate, and yet another filtration, the strontic chloride was converted into carbonate by means of purified ammonic carbonate (see "Ammonic Carbonate"). After a very complete washing the strontic carbonate was dissolved in pure nitric acid in a platinum dish. The nitrate was crystallised, dried at 150°, re-crystallised, washed with alcohol with the aid of the pump, dried, dissolved, and stirred with a little pure strontic carbonate for a week. The filtrate containing pure strontic nitrate was diluted, brought to boiling in a platinum dish, and poured in a fine stream into a boiling solution of pure ammonic oxalate (see "Ammonic Oxalate") also contained in platinum. The strontic oxalate was washed with the purest water upon the filter-pump, until no ammonia could be detected upon boiling the filtrate with sodic hydroxide. Nessler's reagent still showed a trace of ammonia; but since this could easily be expelled by ignition, and the precipitate was very hard to handle, the washing was not carried further. After drying and powdering, the oxalate was converted into carbonate by ignition at a full red heat. The product was now ground in a mortar with an equivalent amount of pure ammonic bromide (see "Ammonic Bromide"), and the whole was gently ignited in a large platinum dish until no more ammonia was evolved. The 100 grms. of strontium bromide thus obtained formed a pure white translucent cake upon fusion in a large platinum crucible. The cake was dissolved in water, and the alkaline solution, after having been boiled for some time, was neutralised with sulphuric acid. The clear filtrate from the strontic sulphate was now evaporated to a volume of about 120 c.c., and diluted with 200 c.c. of the purest alcohol. The mixture was allowed to stand for a day, in order that the strontic sulphate and any trace of baric sulphate which might remain should be precipitated, and then filtered. After three successive crystallisations from water, the substance was used for Analysis 10; a further crop of crystals from the purest mother-liquor served for Analysis 11.

Considering the pains taken in the purification of even the least pure sample, it is not surprising that all of these samples gave quantitative results which proved them to be essentially identical.

Silver.—The preparation of pure silver has been repeatedly detailed. The most elaborate method described in the paper upon barium was used in the present case (*Proc. Amer. Acad.*, xxix., 64, 65). A few improvements were introduced, notably the purification of the sodic hydrate used for the reduction of the argentic chloride by means of a strong galvanic current, instead of by hydrogen sulphide. Little but iron was found in it, however. The final crystals of electrolytic silver were usually fused upon pure sugar charcoal or lime, in a reducing flame; once, however (for Analysis 10) the crystals contained in a lime boat within a stout porcelain tube were fused in a Sprengel vacuum by means of a Fletcher furnace. Two holes bored through the furnace at right angles to the flame entrance served to admit the tube. The heat was very gradually applied, and after the silver had been melted all the apertures of the furnace were closed and the tube was allowed to cool very slowly. A wide glass tube set into the porcelain tube on one end served as a convenient window for the observation of the fusion.

Ammonic Carbonate.—Two varieties of ammonic carbonate were used for the work just described. The first consisted of ordinary pure "ammonic carbonate," which had been dissolved, treated with a small amount of a pure strontium salt, and filtered. This treatment undoubtedly removed any substance which could seriously interfere with the preliminary purifications for which this ammonic carbonate was used. For the final stages of the purification of the strontium preparations, ammonic carbonate was made by saturating the purest water in a platinum vessel with ammonia gas obtained by boiling the pure strong ammonia of commerce, and then passing into this saturated solution pure carbon dioxide. This latter gas was prepared by the action of dilute nitric acid on marble; it was purified by passing through washing flasks containing water and a meter of glass tube packed with moist beads. Upon delivering the gas into a Bunsen flame, no trace of calcium could be detected spectroscopically. Both gases were conducted into the solution through a platinum tube made for the purpose. The resulting ammonic carbonate undoubtedly contained more or less of the amines common in ordinary ammonia, but it could not have contained a trace of non-volatile impurity capable of contaminating the strontic carbonate for whose preparation it was designed.

Ammonic Oxalate.—This salt was made by neutralising pure ammonia water with pure oxalic acid, which had been still further purified by many re-crystallisations from hydrochloric acid and water. The ammonic oxalate was crystallised twice in a platinum dish, the crystals being thoroughly washed each time. The salt was wholly free from chlorine.

Ammonic Bromide was prepared in the usual fashion from ammonia prepared in platinum and bromine purified according to Stas. The reaction was naturally conducted in a flask of hard glass; but the crystallisation was carried on as usual in platinum. A slight excess of the pure white substance precipitated 3·97970 grms. of argentic bromide (fused, reduced to the vacuum standard) from a solution containing 2·28616 grms. of pure silver. From this experiment AgBr : Ag = 100 : 57·4455. Stas found 57·445, hence the purity of the ammonic bromide is proved.

A very simple and convenient platinum condenser was used for the preparation work described above. The tube, almost a centimetre in diameter, and perhaps twenty-five centimetres in length, is bent, somewhere contracted near one end, and surrounded with a condenser jacket. It is easy to draw out the neck of a round-bottomed flask to fit outside of the conical end, and if the juncture is not absolutely tight a thin film of condensed liquid soon makes it so. If the glass neck be prolonged somewhat above the point of juncture, evaporation from this film is very slow. Of course pure filter paper may be used to tighten the joint if water is to be distilled. The apparatus has the great advantages of cheapness and transparency over the ordinary platinum still. All the hydrochloric, hydrobromic, sulphuric, and nitric acids, water, and alcohol used in the important stages of the work were distilled with the help of this contrivance.

Platinum vessels have been used wherever it was possible to use them in the work detailed above, although the fact is not always mentioned. They were cleaned in the usual fashion.

(To be continued.)

NOTE ON THE

FORMATION OF CITRIC ACID BY THE OXIDATION OF CANE-SUGAR.

By ALFRED B. SEARLE and ARNOLD R. TANKARD.

IN the CHEMICAL NEWS (lxxi., p. 296) Dr. T. L. Phipson announces the formation of citric acid by the action of potassium permanganate, at 25° C., on cane-sugar in aqueous solution containing free sulphuric acid. We have carefully followed the directions given by Dr. Phipson, and, like him, obtained no precipitate on adding calcium chloride to the cold neutralised liquid resulting from the treatment with permanganate, but on boiling a copious white precipitate was thrown down.

The precipitate obtained by us differed from that described by Dr. Phipson in the fact that it consisted wholly of hydrated calcium sulphate. Thus, the precipitate, after washing with hot water and drying at 100° C., lost 20 per cent of water on ignition, and did not darken during the process. The residue was not alkaline to litmus, and did not effervesce with acid. It contained sulphate and calcium in the proportions required by the formula $CaSO_4$.

When the precipitate produced by calcium chloride was treated with dilute sulphuric acid, and the filtered liquid concentrated somewhat, small but well-formed crystals were obtained; but analysis and microscopical examination showed that they also consisted entirely of hydrated calcium sulphate, $(CaSO_4.2H_2O)$.

On treatment with boiling acetic acid the precipitate dissolved somewhat, but the precipitate produced by neutralising this solution with ammonia and boiling consisted entirely of hydrated calcium sulphate.

In order to avoid any confusion from precipitation of calcium sulphate, we have also employed nitric acid instead of sulphuric acid for acidulating the cane-sugar solution. In this case we obtained no precipitate on addition of calcium chloride to the neutralised liquid, even on boiling, showing that no citric acid had been formed by the treatment with permanganate.

We have also added potassium permanganate to a solution of sodium sulphite, acidulated with sulphuric acid, until the colour was no longer discharged. The clear liquid was neutralised by ammonia, and calcium chloride added. On boiling the liquid a copious white precipitate was thrown down, but this evidently could have contained no citrate.

We are reluctant to believe that so experienced a chemist as Dr. Phipson would mistake a precipitate of calcium sulphate for one of calcium citrate, but it is evident that the essential conditions must be described more precisely before other chemists can repeat Dr. Phipson's experiment with success.

67, Surrey Street, Sheffield.
July 13, 1895.

MONAZITE — A MINERAL CONTAINING HELIUM.

By ALBERT THORPE.

The following figures represent the results of a recent analysis of a sample of monazite from North Carolina:—

Lanthanum oxide	23·62
Cerium oxide	25·98
Thorium oxide	18·01
Phosphoric acid	28·43
Tin oxide	1·62
Manganous oxide	1·33
Lime	0·91
	99·90

As this mineral is known to contain helium, the above results of a careful analysis may be of interest to the readers of this journal. Due to the far-reaching researches of Ramsay, it is probable that chemists may find coronium and the primordial "material" in some of the rarer minerals, and the "lavas" ejected from active volcanoes.

ON CERTAIN PHENOMENA OBSERVED IN THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF POTASSIUM ANTIMONYL TARTRATE.*

By J. H. LONG.

I have elsewhere called attention to the behaviour of solutions of tartar emetic when treated with solutions of other salts (see *Am. Journ. Sci.*, Oct., 1889, and Oct., 1890), and with Mr. H. E. Sauer have determined the conditions of precipitation by carbonates, acetates, and phosphates (*J. Anal. Appl. Chem.*, March, 1891).

When to solutions of the antimony salt sulphates, chlorides, nitrates, and oxalates of the alkali metals are added no precipitation occurs, even with elevation of temperature. With carbonates, acetates, phosphates, borates, thiosulphates, sulphites, tungstates, and some other compounds, clear solutions can be made at a low temperature, but precipitation follows at a higher point. The precipitate, in nearly all cases, consists of hydrated antimony oxide, and its amount is a function of time, temperature, and amount of added salt.

With mixtures of the tartrate and sodium carbonate, for instance, it was found that in the cold, at the end of twenty-four hours, amounts were precipitated as shown in the following table. In each test 5 grms. of the tartrate were dissolved in 60 c.c. of warm water and cooled to 20°. Then different weights of pure sodium carbonate were dissolved in 35 c.c. of water; these solutions were added to the others and the mixtures were brought up to 100 c.c. They were allowed to stand until precipitation was complete, usually over night or longer. An aliquot part of the clear supernatant liquid was taken and the amount of antimony in solution determined. This was calculated to tartrate in the whole.

No. of experiment.	Na_2CO_3 added.	$KSbOC_4H_4O_6\,\frac{1}{2}H_2O$ left in solution.
	Grm.	Per cent.
1.	0·1	99·93
2.	0·3	85·22
3.	0·5	70·36
4.	0·7	56·76
5.	0·9	40·87
6.	1·2	29·17
7.	1·5	13·94
8.	2·0	3·88

In another series of experiments the solutions of carbonate and tartrate were mixed as before at 20° and then brought to 100°, and maintained at this heat one hour. The precipitates formed immediately, and at the end of the hour were separated by filtration. The filtrates were tested for antimony remaining. The results are shown in the third column below.

No. of experiment.	Na_2CO_3 added.	$KSbOC_4H_4O_6.\frac{1}{2}H_2O$ left in solution.
	Grm.	Per cent.
9.	0·2	79·23
10.	0·5	46·70
11.	0·8	21·74
12.	1·1	8·69
13.	1·5	6·33
14.	2·0	4·42
15.	3·5	4·66
16.	5·0	4·74

On comparing the two tables it will be seen that at first the precipitation is much more rapid in hot solution than in cold, but that finally, with excess of carbonate, a more complete decomposition of the tartrate is effected in the cold solution. Two equations can be given, according to which the reaction may take place. The first of these is—

$$2KSbOC_4H_4O_6 + 2Na_2CO_3 + 2H_2O = \\ = 2KNaC_4H_4O_6 + Sb_2O_3.H_2O + 2HNaCO_3.$$

The second is—

$$2KSbOC_4H_4O_6 + Na_2CO_3 + H_2O = \\ 2KNaC_4H_4O_6 + Sb_2O_3.H_2O + CO_2.$$

The first, probably, takes place in the cold solution, as no carbon dioxide escapes. The loss of carbon dioxide from the hot solution is less than called for by the equation, because an excess of neutral carbonate is present and the solutions are not actually boiled. In any case the precipitation is incomplete, and by addition of increased amounts of sodium carbonate, a condition is reached in which a part of the oxide at first thrown down appears to go into solution again.

Precipitation with sodium acetate takes place imperfectly in the cold, but by heat a stronger reaction follows. In both cases it was found that the results may be expressed by the following equation:—

$$2KSbOC_4H_4O_6 + 2NaC_2H_3O_2 + 2H_2O = \\ = 2KNaC_4H_4O_6 + Sb_2O_3.H_2O + 2HC_2H_3O_2.$$

With phosphates the experiments led to the conclusion that precipitation takes place in a manner represented by this equation:—

$$2KSbOC_4H_4O_6 + HNa_2PO_4 + 2H_2O = \\ = 2KNaC_4H_4O_6 + Sb_2O_3.H_2O + H_3PO_4.$$

With cold solutions precipitation is very slow, but by heat an amount of the antimony oxide corresponding to 75 per cent of the tartrate originally in solution is obtained.

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* *Journal of the American Chemical Society*, vol. xvii., No. 2.

I have since investigated the behaviour of several other salts as precipitants, with the results which follow.

Reaction with Sodium Biborate.

A very sharp reaction takes place between solutions of borax and tartar emetic, which was studied in the following manner. In the first series of experiments 5 grms. of the tartrate were dissolved for each test in 60 c.c. of water, the solutions being brought to 20°. To these were added definite weights of borax dissolved in 30 to 35 c.c. of water at the same temperature. The mixtures were made up to 100 c.c. exactly, and allowed to stand over night in a place with nearly constant temperature. In all cases a precipitate formed which was separated by filtration. The analysis of the precipitate showed it to have the same composition as that formed by the sodium carbonate; viz., $Sb_2O_3.aq$. On drying at a high temperature most of the water is lost, leaving practically Sb_2O_3.

In each case the precipitate was separated by filtration, and the filtrate made up to 250 c.c. 25 c.c. of this was taken and precipitated by hydrogen sulphide, after addition of tartaric and hydrochloric acids in small amount. The precipitation was finished on a hot water-bath, and the precipitate collected on a Gooch filter, washed, dried at 120° and weighed. The sulphide was calculated to tartrate on the supposition that all the antimony in solution was left in the original form ($Sb = 120, O = 16$. The results obtained are shown by these figures:—

No. of experiment.	Borax added.	$KSbOC_4H_4O_6{\cdot}\frac{1}{2}H_2O$ left in solution.
	Grm.	Per cent.
1.	0·1	98·81
2.	0·2	94·74
3.	0·4	87·78
4.	0·8	74·98
5.	1·6	46·84
6.	3·2	3·31

In another series of tests the solutions containing the borax and tartrate were made up to 250 c.c. instead of to 100 c.c. They were allowed to stand, filtered, and treated as before, giving these results:—

No. of experiment.	Borax added.	$KSbOC_4H_4O_6{\cdot}\frac{1}{2}H_2O$ left in solution.
	Grm.	Per cent.
7.	0·1	100·00
8.	0·2	97·15
9.	0·4	89·05
10.	0·8	75·29
11.	1·6	49·09
12.	3·2	6·01
13.	6·4	2·03
14.	12·8	0·99

In a third set of experiments the liquid containing the borax and tartrate was diluted to 100 c.c. in a flask, as in the first set. The flask was closed with a perforated rubber stopper having a long glass tube attached, and then heated in boiling water one hour. The liquid was allowed to cool, was filtered, and the filtrate made up to 250 c.c. An aliquot part, on analysis, gave results which are shown below.

No. of experiment.	Borax added.	$KSbOC_4H_4O_6{\cdot}\frac{1}{2}H_2O$ left in solution.
	Grm.	Per cent.
15.	0·1	99 88
16.	0·2	95·37
17.	0·4	88·81
18.	0·8	74·78
19.	1·6	47·03
20.	3·2	3·96
21.	6·4	1·76

In these tables several things are immediately apparent. It appears that the precipitation is less perfect in hot solution than in cold, although for equal weights of borax the differences are not great. It is seen also that the amounts precipitated are greater in the strongest solutions. These effects of temperature and concentration are far less marked, however, with borax precipitation than with that by the sodium carbonate.

With borax we have, in each case, a very regular rate of precipitation. By platting the weights of borax in the above table as abscissæ, and the amounts of tartrate left as ordinates, we obtain a curve which is almost a straight line.

It seems practically impossible to precipitate all the antimony by excess of borax, although the amount left in solution is much less than when sodium carbonate was used as the precipitant. Direct trials showed that the solubility of the antimonous oxide in excess of borax solution is very slight, but is a trifle greater in the excess of sodium carbonate. The solubility in the Rochelle salt solution formed in the latter case will not account for this difference, as will appear below.

In order to gain further insight into the reaction I measured the amount of rotation of polarised light in a number of solutions before and after the separation of the precipitate of antimonous oxide. Some exceedingly interesting results were obtained, a few of which will be explained in detail. I dissolved 5 grms. of the tartrate in 50 c.c. of hot water and added 3 grms. of borax in 25 c.c. of water, made up to 90 c.c., and heated half an hour in the water-bath. The solution was allowed to cool to 20° and made up to 100·5 c.c. (on account of volume of precipitate), and filtered through a dry filter. The filtrate was polarised in a 200 m.m. tube giving

$$\alpha_D = 3{\cdot}596^{\circ}.$$

Seventy-five c.c. of the filtrate, after the addition of a little hydrochloric and tartaric acids, was precipitated by hydrogen sulphide. The precipitate was collected, washed, and dried in the usual manner in the Gooch funnel. I found 0·119 grm. of the sulphide, corresponding to 0·312 grm. of $KSbOC_4H_4O_6.\frac{1}{2}H_2O$, in the whole filtrate. 4·688 grms. had, therefore, been precipitated. From the outset it would naturally occur to one that the precipitation of antimonous oxide must be accompanied by the formation of sodium potassium tartrate, and that the polarisation effect observed must, in part, be due to this as well as to the potassium antimonyl tartrate left. I have elsewhere given the results of very accurate tests in which the rotation constants of these tartrates were determined by the use of the large Landolt-Lippich polarimeter with the 400 m.m. tube (*Am. Jour. Sci. and Arts, loc. cit.*) From these it appears that the rotation of 0·312 grm. of the $KSbOC_4H_4H_4O_6.\frac{1}{2}H_2O$, and 3·982 grms. of $KNaC_4H_4O_6.4H_2O$ (this latter corresponding to the tartar emetic decomposed) in 100 c.c. should not be over 2·6°. In the direct polarisation of the filtrate I found, as given above, 3·596°. It is evident, therefore, that something else must be present to modify the result.

It is well known that the presence of boric acid increases the rotation of tartrates in a marked degree, and this can be readily accounted for here if we assume that the reaction takes place according to the following equation:—

$$2KSbOC_4H_4O_6+Na_2B_4O_7+6H_2O= \\ =2KNaC_4H_4O_6+Sb_2O_3+4H_3BO_3.$$

On applying tests for free boric acid its presence was readily shown. We have here apparently a reaction similar to those in which acetic and phosphoric acids are liberated from acetates and phosphates.

In the last experiment it was shown that antimony, corresponding to 0·312 grm. of the potassium antimonyl tartrate was still in solution, or that 4·688 grms. had been decomposed. To do this according to the above equation would require 2·697 grms. of crystallised borax, and would leave in solution 3·982 grms. of $KNaC_4H_4O_6.4H_2O$ and 1·751 grms. of H_3BO_3. An excess of 0·303 grm. of borax would be left in solution. To test the correctness of this view I prepared a solution containing in 100 c.c., at 20°—

0·312 grm. of $KSbOC_4H_4O_6.\frac{1}{2}H_2O$,
3·982 grms. of $KNaC_4H_4O_6.4H_2O$,
1·751 grms. of H_3BO_3,
0·303 grm. of $Na_2B_4O_7.10H_2O$.

This solution was polarised in the 200 m.m. tube, and gave—

$$\alpha_D = 3{\cdot}590^\circ,$$

which agrees very well with the result of the first experiment. Another solution, containing in 100 c.c., at 20°—

0·150 grm. of $KSbOC_4H_4O_6\,\frac{1}{2}H_2O$,
4·119 grms. of $KNaC_4H_4O_6.4H_2O$,
1·811 grms. of H_3BO_3,

gave $\alpha_D = 3{\cdot}661^\circ$. While boric acid increases the rotation of tartrates and tartaric acid, I have elsewhere shown that borax decreases the rotation of Rochelle salt slightly. The equation probably represents the facts properly.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

International Catalogue Committee.

The following Report was presented to the President and Council on July 5th; the recommendations contained in it were approved of, and the Secretary was directed to send copies to the several correspondents, and to certain scientific papers:—

Report.

At the first meeting of this Committee (February 8, 1894) the Memorial to the President and Council (July, 1893) which led to the appointment of the Committee, and the Minute of Council of December 7, 1893, appointing the Committee, having been read, it was resolved to request the President and Council to authorise the Committee to enter directly into communication with societies, institutions, &c., in this country and abroad, with reference to the preparation, by international co-operation, of complete subject and authors' catalogues of scientific literature.

Subsequently a draft circular letter was prepared, which, on February 22, 1894, received the approval of the President and Council, who also authorised its issue.

This letter was sent to 207 societies and institutions selected from the exchange list of the Royal Society, and to a few others. It was also sent to the Directors of a number of Observatories and of Government geological surveys, to the Foreign Members of the Royal Society, as well as to those of the following Societies:—Chemical, Geological, Physical, Royal Astronomical, Linnean, Royal Microscopical, Entomological, Zoological, Physiological, and Mineralogical, and of the Anthropological Institute. A special letter was addressed to the Smithsonian Institution.

More than a hundred replies to the letter have been received; several of these are reports of committees specially appointed to consider the suggestions put forward by the Royal Society. A list of answers received up to December, 1894, with brief excerpts from the more suggestive, was issued to members of the Committee early in this year. It should, however, be added that from some important institutions no answer has as yet been received.

It may be said at the outset that in no single case is any doubt expressed as to the extreme value of the work contemplated, and that only two or three correspondents question whether it be possible to carry out such a work. It is a great gratification to the Committee that the matter has been taken up in a most cordial manner by the Smithsonian Institution, the Secretary of which, in his reply, refers to the desirability of a catalogue of the kind suggested as being so obvious that the work commends itself at once. The importance of having complete subject catalogues, and not mere transcripts of titles, is also generally recognised.

Some bodies and individuals take the matter up very warmly, and urge that steps be taken forthwith to put the scheme into action, this being especially true of the replies received from the United States; others, while giving a general approval, dwell upon the difficulties of carrying out the suggestions put forward; and others, again, ask for more details before committing themselves to any answer which may seem to entail future responsibility, especially of a financial character.

Incidentally it may be pointed out as very noteworthy that over and over again reference is made to the great value of the Royal Society's "Catalogue of Scientific Papers." There is abundant evidence that considerable use is made of this on the Continent of Europe. And it is clear that a proposal to carry out a more comprehensive scheme initially under the direction of the Royal Society of London is likely to meet with general approval, owing to the fact that the Society is credited with having already carried out the most comprehensive work of the kind yet attempted. Indeed, the Academy of Natural Sciences of Philadelphia, U.S.A., directly advocates the establishment of a central bureau under the Royal Society; and several others more or less clearly imply that they would favour such a course.

Over and over again, it is stated that the production by international co-operation of a catalogue such as is contemplated is not only desirable, but practicable. The Americans, who, as already stated, are the most enthusiastic supporters of the scheme, especially dwell on the importance of early action being taken. Prof. Bowditch, of Harvard University, in particular, points out that if the Royal Society of London wish to guide the enterprise, it ought to announce its views and put forward a comprehensive scheme with the least possible delay. It may be added here that he also urges that in determining the scope of the catalogue a very wide interpretation should be given to the word "Science."

No very precise information as to the best mode of putting the scheme into operation is to be gathered from the replies as a whole.

It is generally agreed that the enterprise should be an international one. Many think that international financial support should and would be accorded to it, but no method of securing this is indicated; others express the view that the cost may be met by subscriptions from societies, libraries, booksellers, and individuals, without Government aid; and this is perhaps, on the whole, the prevailing feeling among those who have discussed the matter from a financial point of view. But in no case is any attempt made to form any exact estimate of the cost.

A number of scientific bodies and institutions express themselves prepared to work in such a cause. The Secretary of the Smithsonian Institution suggests that, as the Institution receives all the serials and independent works published in America, a branch-office might be established there, and that it is not impossible that a sum of money might be given yearly in aid. The Royal Danish Academy is willing to render as much assistance as possible. It would charge an official of one of the Danish chief libraries in receipt of all Danish publications with the task of editing slips, and would defray the cost of this work. The Société des Sciences of Helsingfors would furnish the Central Office with information as to the scientific work done in Finland. The Kongl. Vetenskaps Akademie of Stockholm would organise a Committee for Sweden.

As regards language, there appears to be more unanimity than could have been expected. Over and over again the opinion is expressed that English should be the language of the subject catalogue. Frequent reference is made to the importance of quoting titles in the original language, although some suggest that this should be done only in the case of those published in English, French, or German, and perhaps Italian.

Some form of card catalogue appears to be generally favoured, especially in America, as the basis of the scheme; the Committee of Harvard University, whose reply is very full, in particular discuss this point in detail.

In an interview with the Committee in March last, Prof. Agassiz spoke very warmly in favour of the scheme, and of the support which it would meet with in the United States, especially from libraries. As others have done, he strongly urged that the co-operation of booksellers and authors should be secured. Prof. Agassiz also expressed the view that the regular issue to libraries and scientific workers from the central office of cards or slips which would afford the material for the construction of card catalogues would form an important source of income, at all events in his country.

From various sides it is urged that an International Congress should be held to discuss plans. This is advocated as a first step in a reply received from the Königl. Gesellschaft der Wissenschaften in Göttingen, a reply to which, not only as regards this point, but also in respect to the whole matter, the Committee attach very great weight, since it embodies in an official form views arrived at by the Academies of Vienna and Munich, and by the scientific societies of Leipzic and Göttingen, who have considered the matter in common. Prof. Agassiz strongly urged the calling of a Conference; and, among others who share this view, Dr. Gill, of the Cape Observatory, in his letter particularly dwells on the great value of such meetings as the means of securing unanimity of action.

Such being the tenor of the correspondence, your Committee are convinced that initial steps of a definite nature in furtherance of the scheme ought now to be taken.

They accordingly request the President and Council to take measures with the view of calling together, in July of next year (1896), an International Conference, at which representatives of the several nations engaged in scientific work should be invited to attend, with the view of discussing and settling a detailed scheme for the production by international co-operation of complete authors' and subject catalogues of scientific literature.

London will probably be found the best place in which to hold such a Conference. It may be desirable to summon the representatives of the different countries through their respective Governments, and it will obviously be necessary that a detailed scheme be prepared, to serve as a basis for discussion at the Conference. These and other points will require much consideration before any action at all can be taken; meanwhile it is desirable that a beginning should be made during the autumn, before the winter session of the Society. The Committee therefore recommend that the President and Council should give the Committee (which includes the President and Officers) executive powers in order that they may take, in the name of the Society, such steps as they may think desirable with the view of calling together the above-mentioned Conference.

Determination of Sulphur in the Leads of Commerce and in Work-lead.—W. Hampe (*Chemiker Zeit.*).—The author describes two methods:—(*a*) Combustion of the specimen in a current of dry chlorine, and employs two receivers filled with water containing hydrochloric acid. (*b*) The oxidation of the lead is effected by means of melting saltpetre, and the sulphuric acid formed is determined. The reagents must be very carefully tested for sulphuric acid. Hampe's results place it beyond doubt that copper may contain copper semi-sulphide even in presence of oxygen.

NOTICES OF BOOKS.

The Manufacture of Explosives. A Theoretical and Practical Treatise on the History, the Physical and Chemical Properties, and the Manufacture of Explosives. By Oscar Guttmann, Assoc. M. Inst. C.E., F.I.C., Member of the Societies of Civil Engineers and Architects of Vienna and Budapest, Correspondent of the Imperial Royal Geological Institution of Austria, &c. In Two Volumes, 8vo. Vol. I., pp. 348; Vol. II., pp. 444. London: Whittaker and Co. 1895.

The author of this thorough-going work makes in his Preface a somewhat alarming statement. The book, he tells us, "is written for manufacturers and experts alone, and anarchists and such like will find nothing new in it." This sentence is certainly open to the construction that anarchists, dynamitards, &c., are, to say the least, fully equal to manufacturers and experts in their knowledge of high explosives. If this is true—and we are not in a position to contravert it—"pity 't is 't is true."

The first subject taken up is that of new materials. Here it is not without interest to note that diversities of opinion prevail concerning the best method of preparation, even in case of so anciently known a substance as charcoal. Another interesting fact is the case of a workman secretly drinking about half a pint of glycerin every day, because the burning in the stomach gave him the same sensation as brandy. This fact may throw a light upon the unaccountable disappearance of glycerin sometimes complained of in print- and colour-works.

The preparation of nitric acid for the manufacture of explosives is given in detail. The sale of this acid by specific gravity is shown to be untrustworthy, especially if the scale of Baumé is used, since "an exact definition of this hydrometric scale does not exist." It is remarked that it is becoming more and more the custom to designate commercial nitric acid in a rational manner, namely, by the percentage of pure nitric monohydrate which it contains.

The general properties of explosives are discussed in the second chapter. They are classified by Colonel Hess into low or direct explosives (ordinary gunpowder being the type), and high or indirect explosives (the type gun-cotton), the highest effect of which is obtained by means of an intermediate agent.

The views of Berthelot, and their criticism by Sir F. Abel and Nobel, are given, and in addition we have certain fantastic methods for increasing the force of gunpowder, dating back to the year 1563. Tables are given showing the composition of gunpowder at different times and in different countries. The manufacture and the properties of prismatic and compressed powders are described and illustrated. There are also a number of powders in which potassium nitrate is partially or entirely replaced by other nitrates, or by potassium chlorate. The number of powders in which some other substance is substituted for charcoal is wonderful, though in most cases with no definite advantage.

The points to which attention is directed in the examination of powders are external condition, solidity of grain, size of grain, density as ascertained with a variety of densimeters, hygroscopic properties, and determination of moisture. Then follows the determination of the various ingredients.

Next we have an examination of what are called the mechanical properties of the powder, viz., the inflammability (it being shown, according to the experiments of Dr. Dupré, that there is scarcely any explosive which will not explode if spread in a thin layer on a wooden floor, and struck a glancing blow with, *e.g.*, a broom-handle), rapidity of ignition, combustion, and products of combustion.

The second volume opens with the manufacture of gun-cotton, and its treatment from every point of view.

It is followed by picric acid and the picrates. Picric acid re-melted seems to be the much-vaunted "melinite" of the French, known in Britain as "lyddite." Picric acid in contact with the metal walls of projectiles seems to undergo changes which interfere with its stability. In its place sodium, potassium, and ammonium picrates have been proposed. A mixture of 432 parts of ammonium picrate with 568 parts of potassium nitrate is under examination on behalf of the French Government.

Trinitro-cresol is used in France, under the name of cresylite, for filling shells and torpedoes, and is ignited by means of a gun-cotton primer.

In Austria the ammonium salt of trinitro-cresol is used under the name of "ecrasite," and is said to be twice as powerful as dynamite.

Blasting-gelatin is a solution of soluble gun cotton in nitroglycerin, and has the advantage of being less susceptible to mechanical shocks than dynamite; but its manufacture is not at all easy.

Cordite, which has recently obtained political notoriety, is made by adding 58 parts nitroglycerin to 37 parts gun-cotton and 5 parts of vaselin. The accidents with this compound which have occurred at Waltham Abbey do not seem due to any defect in the composition.

A point which does not seem to have been made sufficiently prominent concerns the propagation of the shock from explosions of the higher explosives. This takes place not merely through the air, but through the earth. Thus, at the gun-cotton explosion at Stowmarket, the windows of houses at the distance of a mile from the magazine, and looking in the opposite direction, were seen falling out of their frames *before* the noise of the explosion had reached the spot. Hence belts of trees, traverses of earth, &c., are no complete protection against the effects of explosions.

This work commends itself most strongly to all manufacturers and users of explosives, and not less to experts, who may be called on to examine the causes and results of disasters of the kind in question.

Petroleum: its Development and Uses. By R. Nelson Boyd, Member of the Institution of Civil Engineers. Whittaker and Co. 1895. Crown 8vo., pp. 85.

We have here a most useful manual of the origin, composition, properties, and uses of mineral oils. On many of these points consumers and dealers are lamentably ignorant—an ignorance greatly to be regretted concerning an article so valuable, if rightly used, so perilous in careless hands, and introduced into trade in such enormous quantities. We learn here that the imports of "petroleum oils" into the United Kingdom in 1893 reached a total of 155,126,667 gallons, whilst in addition 20,000,000 gallons of oils are obtained from the shales of Scotland.

The number of accidents due to petroleum lamps badly constructed or foolishly managed is very serious, and if we consider that as much as 4,000,000 gallons have been stored at one time at a single wharf in London there is always a possibility of a conflagration on a gigantic scale. Concerning its storage and safe-keeping British law is singularly lax. There is no regulation as regards the quantities which may be stored at or near one place; nor, apparently, as to the construction and security of the magazines. It is indeed enacted that the oil kept for sale must have a flashing-point of 73° F. close test. It is generally admitted by practical men that this point is too low for public safety. In Russia the standard fixed is 82°; in India, 110°, on account of the high temperature to which the oil may be exposed. Germany ventures upon a lower standard than our own, *i.e.*, 70°. If this figure is really degrees Fahrenheit, and not Centigrade, we cannot help feeling surprised.

A very important point to which the author invites consideration is the supply of petroleum. At present our imports are almost exclusively derived from the United States and from Russia. There is here an element of danger, since the consumer may suddenly find the cost price raised by dint of combinations. It is therefore very important that other sources should be sought for, and, if practicable developed. Mr. Boyd mentions here Mexico, Venezuela, and the La Plata regions. In addition, there is Burmah, Java, and Borneo. The use of heavy mineral oils and of petroleum residues for heating engines is a sober reality which deserves to be kept in view as a countercheck to the manœuvres of the coal merchants and the unions of the coal miners.

The origin of petroleum is duly discussed. The theories of its inorganic origin, as advocated by Professors Berthelot and Mendeleeff, are now generally laid aside in favour of the view of Bischoff, that all the mineral hydrocarbons are produced by the decomposition of organic matter, of vegetable origin in Pennsylvania, and of animal origin in Canada. It is now concluded to have been formed, not by destructive distillation, but at the normal temperatures of the earth.

The fact that petroleum is often accompanied by brine is not fully explained. The heaviest mineral oil here mentioned is that of Baku (sp. gr. 0·954), and the lightest that of Pennsylvania (0·730).

This excellent little work is furnished with appendices showing the percentages of theoretical heat converted into useful work by different motors; the flashing-points of mineral oils permitted in different countries; the suggestions as to the construction and management of petroleum lamps issued by the London County Council, but not extending to "benzoline" lamps; thermic values of different mineral oils; and import duties on petroleum in foreign countries and throughout the British Empire. We find that, except the home kingdoms and India, mineral oils are nowhere admitted free.

Chemistry, Organic and Inorganic, with Experiments. By Charles Loudon Bloxam. Eighth Edition. Re-written and Revised by J. Millar Thompson, Professor of Chemistry, King's College, London, and Arthur G. Bloxam, Head of the Chemistry Department, the Goldsmiths' Institute, New Cross, London. London: J. and A. Churchill.

The work before us, which has now reached its eighth edition, is an excellent specimen of what we may call the intermediate type of chemical treatises. It does not aspire to the encyclopædic character of such works as those of Roscoe and Schorlemmer, Watts, and others, but, on the other hand, it avoids the bald fragmentary character of the manuals written in accordance with some syllabus.

The subject-matter has been modified in accordance with the present state of science. Argon and helium have been duly noticed, as far as their properties are already determined. Hydrazine and its derivatives are considered on p. 16. The periodic classification of the elements is expounded; so, likewise, are the fundamental principles of thermo-chemistry, the static method of measuring chemical energy, mass action, the kinetic theory of gases, and dissociation. Such matter, the theoretical aspect of the science, has been placed after the consideration of the non-metallic elements.

After each group of metals there follows a general review of its constituents.

In organic chemistry, the usual division of the substances discussed into fatty and aromatic derivatives has not been retained.

Under the physical properties of organic compounds we find mention of the absorption-spectra, which are thus mentioned detached from the general view of spectrum analysis on p. 303.

The respective applications of chemistry, inorganic and organic, are very fairly explained as far as the bulk of the work can allow.

The rare earths are not ignored, as is too frequently the case, though the elementary character of some of them is not regarded as fully established.

A few oversights cannot escape notice. Thus, in speaking of the Stephenson and Davy safety-lamps—recognised as not absolutely trustworthy—it is mentioned that a Davy lamp may show as little as 0·25 per cent of fire-damp, whilst on the next page (p. 109) we find it observed that "the Davy lamp will not indicate less than 2 per cent."

The sources of diamond are said to be Golconda, Borneo, and Brazil, though the two former deposits are nearly exhausted, and all three together yield a much smaller supply than does South Africa.

Absinthe is mentioned without any due condemnation of its use.

Passing over, however, such trifling omissions, we must pronounce Bloxam's work to be deserving of the full confidence of teachers and students.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Zeitschrift fur Analytische Chemie.
Vol. xxxiii., Part 5.

New Apparatus for Evolving Sulphuretted Hydrogen.—F. W. Küster (*Journ. Prakt. Chemie*).—This paper requires the accompanying cut.

Vacuum Desiccation Apparatus.—L. Storch (*Ber. Oesterr. G.* and *Zeit. Angew. Chemie*).—This paper cannot be intelligibly reproduced without the illustration.

New Apparatus for Extraction.—H. W. Wiley.—*Journ. Anal. and Appl. Chemistry.*

Trustworthy Still-heads.— Max Müller and also L. L. de Koninck.

Determination of Ammonia by Distillation.—Fr. Stolba (*Chemiker Zeitung*).

Washing-bottle for Gases.—J. Habermann (*Zeit. Angew. Chemie*).

Absorption Apparatus for Determining Sulphur in Iron and Steel.—E. M. (*Stahl und Eisen*).

Fixed Absorption Receiver for Permanent Use.—Kenneth Mackenzie (*Journ. Anal. and Appl. Chemistry*).—All these papers require the accompanying illustrations

Automatic Safety Clamp for the Rider of Balances.—O. A. Richter (a circular issued by the author).—The arrangement is a claw which secures the rider and rises automatically if it has to be taken off or put on.

Use of Glycerin as a Heating Liquid in Soxhlet's Drying Apparatus.—Karl Seubert (*Zeit. Angew. Chem.*).—The author shows that if a solution of common salt is used as a heating liquid, leakages appear, even after a short use. This is a consequence of the galvanic contact of the different metals which occasions decomposition of the sodium chloride and solution of the soldering. Glycerin is free from these disadvantages. The author uses it in a 60 per cent solution, boiling at 108—109°, when the escaping current of air indicates 104°.

Safety Gas Jet.—F. Manoschek (*Dingler's Polytech. Journal*, cclxxxiv., 43).—If the flame is extinguished from any cause the flow of gas is arrested.

New Form of Clay Triangle for supporting Platinum Crucibles. — J. B. Coleman. — From the *Journal of the Society of Chemical Industry.*

Indicators for Use in Titration with Normal Solutions of Sulphide.—P. Williams.—From the Chemical News.

Preparation of Zinc free from Arsenic. — H. Lescœur.—From the *Comptes Rendus.*

Occurrence of Ammonia in Zinc Powder.—F. Robineau and G. Rollin.—This is said to be partially soluble, and can be recognised by treatment with hot water, and tested with Nessler's reagent. In part it exists in combination, and can be liberated by boiling with soda-lye. A product free from ammonia can be obtained by boiling and washing with dilute sulphuric acid (1 : 100). The formation of ammonia ensues on the oxidation of the finest zinc powder in contact with air.

Occurrence of Sodium Cyanide in Potassium Cyanide.—T. B. Stillman. — From the *Journal of Analytical and Applied Chemistry.*

Detection and Determination of Lead in Tartaric and Citric Acids.—R. Warington.—From the *Journal of the Society of Chemical Industry.*

Determination of Chlorine in Commercial Iodine.—F. Ullzer and A. Friedrich.—*Mitt. k. k. Gewerbe Museum* and *Journal of the Society of Chemical Industry.*

Detection of Iodic Acid in Nitric Acid. — Loof (*Apotheker Zeit.* and *Rep. Chem. Zeitung*).—To 5 c.c. of the officinal acid the author adds 0·1 grm. calcium and sodium hypophosphite. If iodic acid is present a colouration appears in a few minutes, and can be made more distinct by means of chloroform.

Preparation of Pure Concentrated Hydrobromic Acid in Quantity.— E. Léger.— From the *Comptes Rendus.*

Volatility of Stannic Chloride.—T. M. Drown and G. F. Eldridge.—From the *Technological Quarterly.*

Presence of Arsenic and Antimony in Ores of the Upper Harz.— W. Hampe (*Chemiker Zeitung*). — Of interest chiefly to chemists and metallurgists of the Harz district.

Attraction of Water by Iodine and Determination of Water in Iodine.—C. Meinecke.—*Chemiker Zeitung.*

Detection and Determination of Alkyl combined with Nitrogen.—J. Herzig and H. Meyer.—The authors observed that the alkyl-iodine derivatives of pyridin and quinolin on heating were decomposed into the bases and the iod-alkyls, and determine the latter according to Zeisel's method. The decomposition is nearly quantitative, and the quantity of alkyl found differs from the calculated amount only by 0·8 per cent.

Separation of Volatile Fatty Acids.—M, Wechsler (*Monats'hefte*).—Liebig found that on the partial neutralisation of a mixture of volatile acids and subsequent distillation, the acid with the higher proportion of carbon passed over first into the distillate, whilst that with the lower proportion of carbon was left behind as a salt. Wechsler has examined in this manner mixtures of formic, acetic, propionic, butyric, isobutyric, isovalerianic, and capronic acids. With one exception (the separation of butyric and isovalerianic acids), the first fraction always contained the pure acid with the higher proportion of carbon, whilst the constituent of the last fraction was the acid poorer in carbon.

Simultaneous Determination of Carbon and Nitrogen.—Felix Klingemann.—The author uses the process proposed by Frankland for the determination of nitrogen.

Determination of Nitrogen in Organic Substances.—A. Petit and L. Moufet.—From the *Journ. de Pharmacie* and *Journal of the Chemical Society.*

Determination of Nitrogen in Nitrates and in Admixture with Organic Nitrogen Compounds.—V. Schenke.—*Chemiker Zeitung.*

Determination of Glycerin.—S. Salvatori (*Staz. Sper. Agrar.* and *Journ. Chem. Soc.*

Atomic Weight of Palladium.—E. H. Keiser and Mary B. Breed (*American Chemical Journal*).—The result obtained was Pd = 106·246.

Determination of Solubility of different Salts.—H. Landau (*Monats'hefte*).—The author proceeds in the same manner as Deszathy, and gives his results in the form of a table.

Determination of Nitrogen in Organic Nitro-compounds, *e.g.*, Nitro-glycerin.—P. Rubtzoff.—*J. Russ. Chem. Soc.* and *Journ. Chem. Soc.*

Determination of the Solubility of Barium and Calcium Butyrate. — A. Deszathy (*Monats'hefte*). — This paper requires the accompanying illustration showing the author's apparatus.

Action of Sodium upon Water.—M. Rosenfeld (*Journal fur Prakt. Chemie*).—Concerning the explosion which occurs under certain circumstances when sodium acts upon water, the author arrives at a conclusion antagonistic to previous conjectures. It was formerly supposed that peroxide was formed, and induced explosion by the development of oxygen. Proceeding on this view, Rosenfeld thought that large quantities of detonating gas might be obtained by passing watery vapour over sodium without the occurrence of explosion. No explosion occurred; but no trace of oxygen accompanied the hydrogen escaping. He considers that "sodium, in its action upon water, whether in open vessels or in those with a water-joint, is dissipated from the interior outwards, as in the phenomenon of spitting; the centre of the explosion lies in the interior of the metal, and the probable cause of the explosion is not the formation of detonating gas, but of a sodium hydride which is suddenly decomposed. The author deduces from his experiment a new method of preparing caustic soda and hydrogen. Sodium is placed in an iron pan, which can be closed with a lid, and watery vapour is introduced. If the access of watery vapour is cut off when the development of hydrogen ceases, we obtain solid caustic soda mixed with finely divided iron. Rosenfeld considers that there is first formed a sodium-iron alloy, which is then decomposed with the liberation of iron. Vessels of silver are also attacked.

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THE CHEMICAL NEWS.

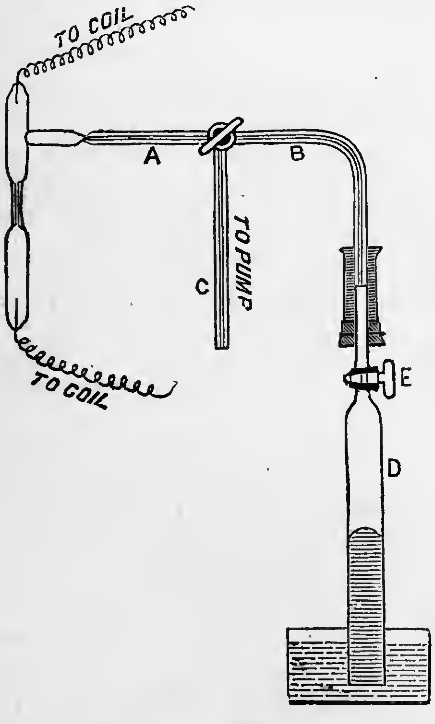
Vol. LXXII., No. 1861.

A METHOD OF TRANSFERRING GASES TO VACUUM-TUBES FOR SPECTROSCOPIC EXAMINATION.

By JAMES YOUNG, A.R.C.S., F.C.S., and
CHARLES R. DARLING, Wh.Sc., A.R.C.S. (Ireland).

While engaged in an examination of the gases evolved by certain minerals, we found it necessary to devise a method of filling vacuum-tubes, using small quantities of gas, so as to recover all excess. The subjoined sketch shows the method adopted, and which we found to be more convenient than any other method we have tried.

A three-way capillary tap has one of its arms, B, bent at right angles. The tube D, containing the gas to be admitted over mercury, and possessing a plain tap, E, is connected to B by means of a mercury joint. Both taps must be perfectly vacuum-tight. The arm C is connected with the Sprengel or other pump, whilst the arm A is fused to the side-piece of the vacuum tube, which latter is made of sufficient length to allow of convenient fusion. After joining to A, the side-piece is drawn out so that it may be readily sealed off after filling. The operation is then conducted as follows:—The three-way tap is turned so as to connect A and C, and pumping continued until as good a vacuum as possible is obtained. The tap E being closed, B and C are then connected, and the space between the two taps pumped free of air. The tap is now turned so as to connect A and B, and the tap E turned on, so as to admit a little of the gas into the vacuum tube. The arms A and C are again connected, and the excess of gas pumped out and collected over mercury at the bottom of the fall-tube, all loss being thus avoided. This process is repeated two or three times to wash out the tube. The tubes may be sparked *in situ*, so that the pumping may be discontinued at any desired moment, and the tube sealed off.



We may mention that in a specimen of samarskite examined the residual gas obtained, after exploding with oxygen (to remove hydrogen and a hydrocarbon present), absorbing with potash, and removing excess of oxygen with alkaline pyrogallol, was found to be pure nitrogen. This was mixed with oxygen, and sparked for a considerable time over potash. There was a steady diminution of volume during the sparking; but at no period could any trace of helium be detected spectroscopically.

Whilst sparking the tubes with a strong current, with a fairly high vacuum, we obtained brilliant mirrors of platinum deposited on the sides of the tube adjacent to the platinum electrodes. This was particularly the case with those containing nitrogen, and when several strands of thin platinum wire twisted together were used as electrodes. With a single piece of thick wire as electrode, only a slight blackening was obtained. With hydrogen and oxygen, using the same current, there was only a very slight deposit in all cases. In the nitrogen tubes, when the deposit attained a certain density, the current flashed across radially from the electrodes, and after a time began to eat away the mirror from the edges, re-depositing a portion of it on the walls of the tube at the dark spaces. At the moment when the mirror began to conduct, a brilliant yellowish-green fluorescence was observed in the glass, which was scarcely visible previously. We have also noticed the phenomenon mentioned by Prof. Ramsay, viz., that with the deposition of the mirrors in nitrogen tubes the gas appears to be carried down by the platinum, a very high vacuum being in some cases obtained, which refused to allow the passage of the current.

Chemical Laboratory, Royal Military Academy,
Woolwich, July 16, 1895.

THE DETECTION OF SULPHATES, SULPHITES, AND THIOSULPHATES, IN PRESENCE OF EACH OTHER.

By R. GREIG SMITH, B.Sc.

The separation of the acids has long been recognised as a matter of great difficulty by chemists and uncertainty by students, and it is with the intention of simplifying the detection of the commonly-occurring sulphur acids that the following method is given. Though it may not be altogether new, the process does not appear to be completely given in text-books on qualitative analysis.

Preliminary testing will probably have indicated the presence of thiosulphate, in which case a dilute solution of the substances under examination must be employed, or a decomposition of the thiosulphuric acid into sulphur and sulphuric acid will speedily take place. Barium chloride in excess is added, together with a good quantity of ammonium chloride, which, like many salts of ammonium, potassium, and calcium, acts as a flocculant or coagulant, and facilitates the filtration of the barium sulphate. Hydrochloric acid is next added, drop by drop, until it is evident that there is no further solution of barium sulphite and thiosulphate, and that only the sulphate remains undissolved; the solution is then filtered through a moistened double filter-paper, which should be free from "pin-holes."

The filtrate will probably be clear; but if not it should be returned to the filter for a second filtration. When too much thiosulphuric acid is present, the clear filtrate will visibly become clouded, or from being whitish will become more opaque: if this occurs the solution should be thrown out, and a fresh portion made more dilute. A solution of iodine is added to half of the filtrate until the colour is of a permanent yellow tinge; a white precipitate indicates the presence of a sulphite which has been oxidised by the iodine to sulphate. In the absence of a decided precipitate, traces of sulphite may be readily detected by comparing the treated and the untreated halves of the filtrate —a procedure which very often saves a good deal of time, as it is unnecessary to wait until a clear filtrate is obtained. The two halves are mixed, and if the yellow colour disappears more iodine is added; the solution is filtered, and the filtrate divided into two halves as before. With a slight turbidity filtration may be omitted. Bromine water is added to one of the halves when any thiosulphate in the original solution shows itself as a white precipitate of barium sulphate, readily seen on comparing the two test-tubes. The thiosulphate is by the iodine converted to tetrathionate, which is oxidised by the bromine water to sulphate. Hydrosulphuric acid would interfere with these reactions, and ought to be eliminated by bubbling carbon dioxide through the solution until the gas escaping from the tube no longer darkens lead-paper.

Durham College ot Science,
Newcastle-upon-Tyne.

THE PRODUCTION OF CYANIDES,

By H. N. WARREN, Research Analyst.

Since the establishment of the cyanide process for the separation of gold from its ores, the race for the production of that compound, in quantity and at cheap rates, has been almost as keen as were the previous attempts to reduce the alluvial deposits, and thus place upon the market the aluminium of to-day. Potassium nitrate, KNO_3, has long been experimented with in the hopes of replacing the oxygen equivalent by carbon, and by so doing produce KCN; but the large percentage of oxygen which is in every case set free at once determines the destruction of any cyanides thus formed, although traces of cyanides are always observed to be present after the partial reduction of commercial nitrates by means of carbon, owing to the secondary action of the ammonia thus formed, due to the moisture present.

Rochelle salt, mixed with a quarter of its weight of potassium nitrite, KNO_2, and ignited, has given 5 per cent as the highest yield of cyanide obtainable, while most hydrated carbonaceous substances yield a still lower per cent. Anhydrous sodium acetate, in admixture with a nitrite, has yielded as much as 30 per cent of alkaline cyanide; whilst in a more recent experiment a mixture of 4 parts of wheaten flour to 1 part of nitrate, and the whole thoroughly mixed with 3 of magnesia and compressed into blocks, yielded, after ignition, from a varying percentage up to 15 per cent of cyanide. The production of sulphocyanides and the reduction of the same by means of lime and carbon, have on several occasions given valuable results in accordance with the following equation:—

$$KCNS + CaO + C = KCN + CaS + CO;$$

but at other times, in consequence probably of the difficulty in regulating the temperature, has resulted in the formation of worthless substitutes.

On returning to the old method for the production of cyanides, by the incineration of nitrogen compounds, a valuable addition will be found in the use of lime or barium oxide; probably both the barium and calcium cyanides are more readily formed than alkaline cyanides; and in lixiviation, in contact with the alkaline carbonates present, they at once form alkaline cyanides and earthy carbonates or ferrocyanides, as arranged for.

Again, potassium and sodium cyanide together are much easier to produce than either separate, fusing at a much lower temperature, and containing more cyanogen, in consequence of the difference in the equivalent of sodium when compared with potassium. A mixture of equal weights of the two alkalis reacts well in every respect, and yields good results.

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

THE DETERMINATION OF URIC ACID, AND OF THE SO-CALLED XANTHIN-SUBSTANCES IN URINE.

By F. HOFMEISTER.

The precipitate obtained, according to Salkowski-Ludwig, on precipitating the uric acid with silver nitrate, contains more nitrogen than correspounds to the uric acid obtainable from the specimen of urine. W. Cameron has utilised this behaviour for an approximate determination of the xanthin-substances. A process indicated by E. Salkowski can be applied for the same purpose.

The silver precipitate obtained (Salkowski-Ludwig) from 500 or 1000 c.c. of urine, after being carefully washed, is decomposed with hydrogen sulphide, and the filtrate is evaporated to dryness and extracted with sulphuric acid at 2 or 3 per cent. The uric acid then remains almost entirely undissolved; it is filtered off, washed, and weighed. The filtrate is rendered alkaline with ammonia, and again precipitated with a solution of silver. The precipitate obtained contains the so-called xanthine-substances along with minimum quantities of uric acid. Salkowski estimates its quantity at 8 to 10 per cent of the weight of the uric acid.

M. Krüger and C. Wolff (*Zeit. Physiol. Chemie*) have obtained in their experiments decidedly higher values (as a mean 0·26 per cent of the weight of the uric acid). Their process is founded on the precipitabilty of uric acid and of the xanthin-bases (Kossel and Krüger name them alloxur-bases) by copper sulphate and bisulphite. 100 c.c. of urine, free from albumen, are mixed when boiling with 10 per cent of a solution of sodium bisulphite, containing, in 100 c.c., 50 grms. of the salt, and immediately afterwards with 10 c.c. of a 13 per cent solution of copper sulphate, and then again heated to ebullition; 5 c.c. of a 10 per cent solution of barium sulphate are then added to promote settlement. After standing for two hours the precipitate is brought on a filter of Swedish paper, completely washed with water which has been previously boiled and cooled down to 50°, and then used, along with the filter, for determining the nitrogen by the Kjeldahl process. The value obtained gives the nitrogen of the uric acid *plus* that of the xanthin-bases. A simultaneous determination of the uric acid by the Salkowski-Ludwig process permits a calculation of the nitrogen belonging to the uric acid. The nitrogen of the xanthin-bases is found from the difference.

A process for determining uric acid, given by Denigés, differs from that of Haycraft only in the manner of titrating the silver. The author uses a process depending on the formation of potassium silver cyanide in an ammoniacal solution, using potassium iodide as indicator.—*Zeitschrift fur Analytische Chemie*, xxxiii., p. 767.

Atomic Weights of Nickel and Cobalt.—Clemens Winkler.—The author has undertaken this re-determination in consequence of the published results of G. Krüss and F. W. Schmidt, and of H. Remmler. These results indicate that nickel and cobalt, as known at present, are contaminated with an unknown element, so that the true nickel and cobalt are not known in a pure state, and their atomic weights are not determined. Winkler gives the atomic weight of nickel as 58·90, and that of cobalt as 59·67.—*Zeitschrift für Analytische Chemie*, vol. xxxiii., Part 5.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending June 30th, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 12th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 166 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 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.

Of the 166 samples examined one was recorded as "slightly turbid," the remainder being clear, bright, and well filtered.

June has been a very dry month. Three-hundredths of an inch of rain fell at Oxford on the 1st, and eight-hundredths on the 11th. With these trifling exceptions no rain fell till the 26th, when there was a downpour of three-quarters of an inch. On the 28th nearly a quarter of an inch fell, followed on the 29th by two-hundredths additional, making a total of 1·12 inch. The mean of 25 years being 2·21, the deficiency is 1·09 inch. Unfortunately neither the river nor the country is much the better for the 1·12 inches falling in June, The bulk of this coming down on two stormy days near together, little time was allowed for the water to sink into the ground. The consequences being, swollen water courses for a few hours, a sudden flood in the river followed by as rapid a subsidence, and little if any permanent good, as compared with what would have been occasioned by the same amount of rain distributed over a greater number of days.

The purity of the Thames-derived waters is now at a very high level, and there is not much room for improvement in chemical quality; but that it is kept up and somewhat improved in all respects, the following table, giving the comparison between the composition of the waters in May and June of this year, is a satisfactory proof.

1895.—*Averages of the Five Supplies derived from the River Thames.*

1895.	Common Salt. Per gall. Means.	Nitric Acid. Per gall. Means.	Hardness. Degrees. Means.	Oxygen. reqd. Per gall. Means.	Organic Carbon. Per gall. Means.	Organic Carbon. Per gall. Maxima.	Colour. Br'n : Blue. Means.
May	1·994	0·908	14·41	0·045	0·128	0·206	13·5 : 20
June	1·951	0·903	13·85	0·034	0·081	0·100	11·4 : 20

Comparing the composition of the waters in June with that of the corresponding month last year shows an almost equally satisfactory result.

Bacteriological examinations of the waters from the general wells of the Water Companies, and from the unfiltered water of the river, have been proceeded with throughout the month. At the works the average number of microbes was 19, and in the river the average was 7625 microbes per c.c. The amount of impurity communicated to the river by a heavy storm following a long drought is shown by bacteriological examinations before and after the heavy storm on the 26th. Before the storm the Thames contained 3230 microbes per c.c., and immediately after the numbers rose to 29,032. This large increase produced no perceptible augmentation of the number of bacteria in the clear water wells of the respective Companies. A careful bacteriological examination of the water at the Companies' works on the days succeeding the storm showed that the filtration was effective, no appreciable increase being detected in the number of microbes present.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

First Paper: The Analysis of Strontic Bromide.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 31).

Method of Analysis.

As in the case of baric bromide (*Proc. Amer. Acad.*, xxviii., 23), the silver required to precipitate all the bromine in strontic bromide was determined, as well as the amount of argentic bromide formed by the precipitation.

The chief problem which presented itself was the preparation of pure dry neutral bromide of strontium for weighing. In preliminary analysis the salt was ignited or fused in a platinum crucible, and weighed as the baric bromide had been. The decomposition of the salt was so great, however, that the uncertainty of the alkalimetric correction sometimes amounted to two or three tenths of a m.grm.; hence this method was clearly inadmissible.

The fusion of the salt in a platinum boat in a stream of nitrogen gave much better results, and two or three further preliminary determinations by this method gave promise of much greater accuracy. It is probable that the slight decomposition which occurred even in the atmosphere of nitrogen was due to the presence at 250—300° of a slight trace of moisture.

The presence of an excess of hydrobromic acid must necessarily lessen or prevent this decomposition; hence in three succeeding determinations (Nos. 13, 14, 15, below) pure dry hydrogen bromide was added to the nitrogen in which the combustion was conducted.

In these cases, however, the platinum boat, which had previously remained quite constant in weight, was evidently attacked, since upon one occasion (Exp. 15) it lost over two-tenths of a m.grm., and the pure white strontic bromide became tinged with a brown colour. The weight of the boat *after* each fusion was taken as the true weight, because the bromide of platinum, if formed, must precipitate nearly as much silver as the bromide of strontium.

In order to avoid the corrosion of the boat, hydrogen was added in small quantities to the mixture of gases. This, by preventing the dissociation of the hydrobromic acid, effectually preserved the platinum, and the boat remained constant in weight. The pure translucent or transparent colourlessness of the fused salt left nothing to be desired. A somewhat complex piece of apparatus was needed for the purpose. (See Fig. 1). A mixture of six volumes of pure nitrogen (made by passing air and ammonia over red-hot copper) and one volume of pure hydrogen was delivered from a gas holder through a succession of tubes of red-hot copper, dilute chromic and sulphuric

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* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*.

acids, concentrated alkaline pyrogallol, and fused potash, into the arrangement for preparing hydrobromic acid. This, as well as all the apparatus following, was without rubber connections, the ground joints being made tight by means of syrupy phosphoric acid (Morley) and flexible by means of fine glass gridirons (Finkener). The pure dry nitrogen and hydrogen were led in the first place into a flask containing bromine, and then over asbestos and red phosphorus saturated with pure fuming hydrobromic acid. The bromine and hydrobromic acid were proved to be pure by the usual quantitative analysis, and the red phosphorus was ground and washed many times with pure water to free it as much as possible from chlorine (Stas). The mixture of pure slightly moist hydrogen bromide, nitrogen, and hydrogen was now dried by calcic bromide free from chlorine and iodine, and thus became ready for use.

The hard glass tube used for heating the platinum boat containing the strontic bromide was ground very tightly into its socket of soft glass, since it was not advisable to risk the presence of phosphoric acid here. The powdered nearly anhydrous strontic bromide, having been packed tightly into the boat and carefully pushed into position in the fusion tube, was thoroughly dried at 200° in a stream of pure air. The elaborate apparatus for preparing the mixture of gases was now connected with the fusion tube, and when all the air had been expelled the boat was slowly heated to cherry-redness until the strontic bromide was wholly fused. The temperature was then allowed to fall a little below 600°, and the solidified bromide of strontium was freed from any possible excess of hydrobromic acid by a current of dry hydrogen and nitrogen free from acid, delivered through a short-cut tube (see Fig. 1).

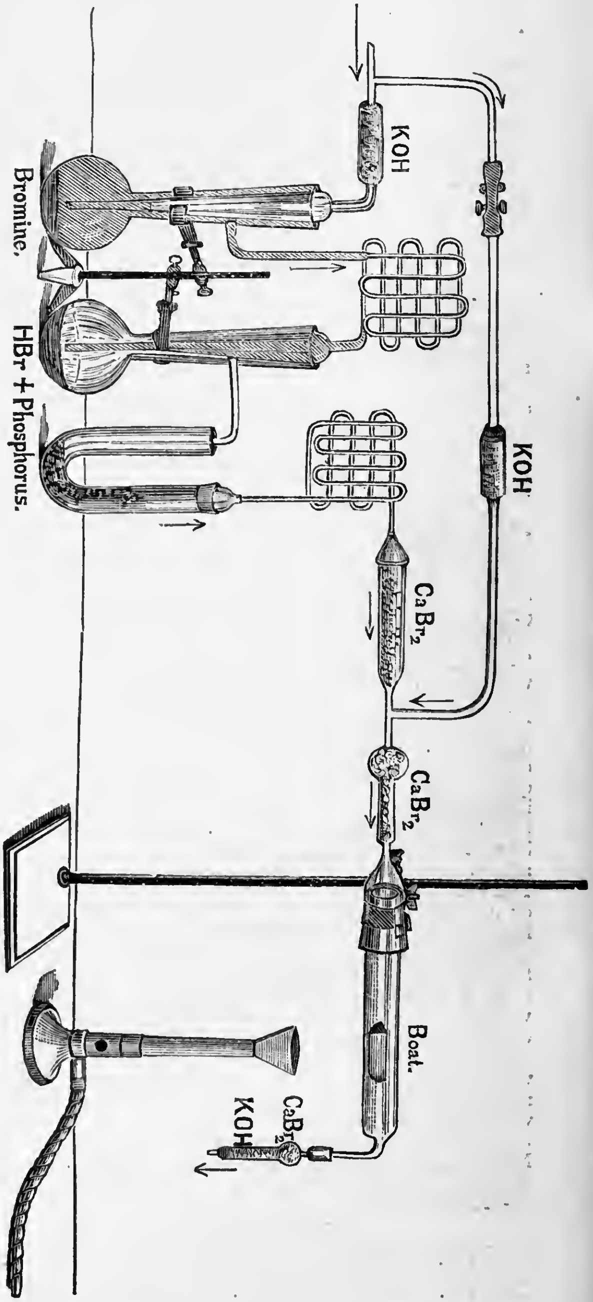

Fig. 1.—Apparatus for Fusing Strontic Bromide.

The almost red-hot boat was now transferred as quickly as possible to the light weighing bottle, within which it was allowed to cool. In the preliminary work (and in Analyses 13 and 14) this bottle was stoppered at once and cooled in an ordinary desiccator. Subsequently an improved desiccator was devised for this purpose. A wide glass tube capable of containing the weighing-bottle was drawn out at one end to a fine tube, which was fitted with a ground glass stopper. The other open end was made slightly conical and ground into a receptacle which was in its turn attached to a drying tube containing fused potash. The accompanying sketch supplements this description (Fig. 2).

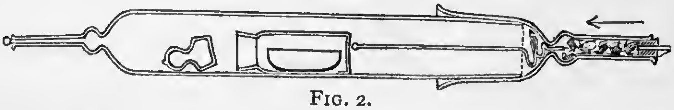

Fig. 2.

While the boat was still hot within the fusion tube, the stopper of the weighing bottle was placed in the horizontal desiccator tube. The moment after the transference of the boat into the bottle, both together were slid into the momentarily opened desiccator tube by means of a glass rod which projected from the receptacle. The bottle was held by means of a glass carriage during this manipulation.

The open weighing bottle, with its stopper and fused contents, could now be heated indefinitely in a current of pure dry air at any temperature below the softening-point of soft glass. At the moment when it was desired to close the bottle, it was only necessary to elevate the desiccator tube from the horizontal to the vertical position, and the hot stopper fell automatically into the equally hot bottle. The desiccator tube was now closed above, and allowed to cool at least four hours in the balance room. It is needless to say that before taking the final weighing of the bottle its stopper was loosened.

Having thus obtained as nearly as possible the true weight of the typical salt of strontium, the remainder of the analysis was conducted in a manner essentially similar to that adopted in the case of baric bromide (*Proc. Amer. Acad.*, xxviii., 24). Since it is unnecessary to describe again most of the precautions, nothing will be noted below excepting those particulars in which the details of the work differed from those already given. Two analyses, which were vitiated by known errors, are omitted from the tables.

(Pure dry nitrogen and hydrogen enter the apparatus through the tube at the left. The arrangement for preparing this mixture is not shown. Upon closing the pinchcock in the upper left-hand corner, the gases are driven through the flasks and charged with dry hydrobromic acid; upon opening the pinchcock, the hydrostatic pressure below causes the gases to flow through the upper short-cut tube and effectually sweep out the acid from the fusion tube. This latter tube, containing the boat in which the strontic bromide is fused, is at the right of the figure).

(To be continued).

ON CERTAIN PHENOMENA OBSERVED IN THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF POTASSIUM ANTIMONYL TARTRATE.*

By J. H. LONG.

(Continued from p. 34).

In the above nothing has been said about certain peculiarities observed in the formation of the precipitates. When cold dilute solutions of borax and the tartrate are mixed no reaction takes place immediately, but with warm strong solutions, a precipitate seems to form as soon as the two liquids are poured together. In a former paper (*Journ. Anal. Appl. Chem., loc. cit.*) I pointed out the important and exceedingly curious fact that in the reaction between carbonates or acetates on the one hand, with the tartrate on the other, while no precipitate may appear immediately, perhaps not in hours, indicating a decomposition, the polarimeter shows that such has taken place. Here, also, we have evidence that a reaction has taken place even without precipitation, and this the polarimeter furnishes. The matter can be best explained by giving the details of several experiments.

I made five solutions by dissolving 5 grms. of the tartrate as before in 55 to 60 c.c. of warm water, cooled to 20°, and added certain weights of borax in small volumes of water, making the solutions finally to 100 c.c. at 20°. These solutions were polarised immediately in the 200 m.m. tube, with the following results:—

No. of expt.	$KSbOC_4H_4O_6.\frac{1}{2}H_2O$ taken.	$Na_2B_4O_7.10H_2O$ added.	α_D.
1	5 grms.	0·5 grm.	12·08°
2	5 ,,	1·0 ,,	9·40°
3	5 ,,	2·0 grms.	5·53°
4	5 ,,	3·0 ,,	4·10°
5	5 ,,	4·0 ,,	3·75°

The normal rotation of the tartrate at 20° in the 200 m.m. tube, with a concentration of 5 grms. in 100 c.c., I have shown to be—

$$\alpha_D = 14{\cdot}103^\circ.$$

The effect of the borax is therefore marked, but the extent of the decrease in rotation depends on the number of minutes intervening between the mixing of the solutions and the completion of the observation in the polarimeter. A gradual decrease in the readings was in all cases observed, until the solutions became finally too turbid for observation from the beginning precipitation. The first solution, for instance, in the above table was read as follows:—

10 hours, 30 minutes, $\alpha_D = 12{\cdot}08^\circ$
10 ,, 45 ,, ,, $= 11{\cdot}87^\circ$
10 ,, 55 ,, ,, $= 11{\cdot}80^\circ$

After standing some hours, the solutions deposited a precipitate and cleared up. On again polarising I found:—

No.	α_D.
1	11·52°
2	9·01°
3	5·29°
4	3·92°
5	3·65°

These observations were made in a 200 m.m. tube, but similar solutions were polarised in a 400 m.m. tube with perfect sharpness, the readings agreeing within 0·02°, as is possible with the large and excellent instrument used. I mention this to prove the perfect transparency of the liquids, and to show that the decreased rotations observed at the start were not due to any loss through precipitation, but were in consequence of changes preceding precipitation, these changes taking place very gradually.

We have here a phenomenon reminding one of the birotation of solutions of certain sugars, but depending on a different cause undoubtedly. In the reaction between the same tartrate and sodium carbonate the same change was observed, but through a longer period. A solution containing in 100 c.c. one-tenth grm. of the carbonate and 5 grms. of the tartrate gave, at the end of five minutes in a 400 m.m. tube, a rotation of 25·582°, after thirty minutes, 25·580°; that is, practically the same; but after twelve hours, 24·480°. A perfectly clear mixture can be made containing 5 grms. of the tartrate and nine-tenths grm. of sodium carbonate in 100 c.c. When polarised immediately, I found with this in the 400 m.m. tube $\alpha_D = 11{\cdot}57^\circ$; after ten minutes, 11·50°; after twenty-five minutes, 11·132°; and after sixty-five minutes, 10·55°.

In the normal reaction between carbonates or borates and the potassium antimonyl tartrate a precipitate should be formed, but we find that at a low temperature this is much delayed. If precipitation alone were taken as the indication of a reaction it would necessarily appear that at the outset no reaction takes place, but the behaviour with polarised light shows the error in this view. It is evident that a reaction begins immediately and progresses far toward completion in some of the cases considered before even the first polarisation can be made; that is, within two or three minutes. This first part of the reaction is the beginning stage of precipitation and may consist in the formation of some intermediate product, which finally decomposes. I have elsewhere shown (*Am. Journ. Sci. and Arts, loc. cit.*) that the rotation of potassium sodium tartrate is decreased by the addition of sodium, thallium, and lithium salts, but is increased by the addition of potassium and ammonium salts, and that this reaction is fully accounted for if we assume the formation of sodium tartrate, sodium-thallium tartrate, or sodium-lithium tartrate in the one case, or of potassium or potassium-ammonium tartrate in the other. In the present instance we evidently must admit the formation of sodium-potassium tartrate from the instant the solutions are mixed, but that the reaction is a progressive one. The potassium antimonyl compound with a high rotation gives place to the potassium-sodium compound with a much lower rotation, There is nothing to show, however, in what form the antimony is held.

Possibly the reaction may be explained by assuming the formation of an intermediate product according to this equation:—

$$2KSbOC_4H_4O_6 + Na_2B_4O_7 = 2KNaC_4H_4O_6 + (SbO)_2B_2O_7.$$

If the last compound is formed it must break up in this manner—

$$(SbO)_2B_4O_7 + 6H_2O + XH_2O = 4H_3BO_3 + Sb_2O_3.XH_2O,$$

leaving a hydrated oxide of antimony with more water than the final precipitate contains. By loss of water, possibly, this hydrated compound must, in time, settle out as a precipitate. It has been explained that, by boiling, the precipitate forms and subsides soon. At 20°, even after what I have called the preliminary stage of precipitation, may have occupied hours, the actual formation of the precipitate may consume an equally long time. The

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* *Journal of the American Chemical Society*, vol. xvii, No. 2.

precipitate is a growth through an invisible and a visible stage, and what is true here is true of the next case to be given.

Reaction with Sodium Tungstate.

Cold solutions of the tartrate give no immediate precipitate when mixed with cold solutions of ordinary sodium tungstate, but on standing the mixtures gradually become turbid, and finally deposit a sediment. The composition of this depends largely on the temperature and concentration. The precipitate formed in the cold, collected, and dried at 105—110° C., consists essentially of antimony oxide. A precipitate formed by mixing hot solutions has practically the same composition, but if obtained after long heating it contains a relatively larger amount of tungstic acid.

In a series of tests made by mixing hot solutions of the two salts, and allowing the mixtures to stand several hours to cool, the following results were obtained:—

$KSbOC_4H_4O_6 \cdot \frac{1}{2}H_2O$ in 100 c.c.	$Na_2WO_4 \cdot 2H_2O$ in 50 c.c.	Weight of precipitate.	Sb_2S_3 from same.	Per cent of Sb in precipitate.
1 grm.	2 grms.	0·3087	0·3467	80·22
2 grms.	2 „	0·6442	0·7291	80·84
4 „	2 „	0·5728	0·6486	80·88
5 „	2 „	0·7222	0·8170	80·79

The mixtures were made in platinum dishes holding about 200 c.c., and as the precipitates formed as a coherent coating on the dishes they were easily washed, dried at 110°, and weighed. They were then dissolved in diluted hydrochloric acid, which left a small amount of tungstic acid in each case in flocculent form. The solutions were then filtered, and, after the addition of some tartaric acid, were precipitated by hydrogen sulphide in the usual manner. The sulphide precipitates were collected on a Gooch, dried at 110°, and weighed. It will be seen that the results are a little low to correspond to pure antimony oxide as the composition of the white precipitate. This compound contains 83·3 per cent of antimony. The compound $Sb_2O_3.H_2O$ contains 78·4 per cent. The lower results are doubtless due to the small amounts of tungstic acid left in each case on treatment with hydrochloric acid, and referred to above.

In a second series of experiments constant amounts of the tartrate in hot solutions were mixed with varying amounts of the tungstate, likewise in hot solution. The white precipitates which formed were collected and weighed as before, with the following results, which show the effect of excess of tungstate on the amount of precipitate. In each case 2 grms. of the tartrate were taken in 100 c.c., and the tungstate in 50 c.c.

Tungstate taken.	Precipitate obtained.
0·5 grm.	0·1070
1·0 „	0·4598
2·0 grms.	0·5762
3·0 „	0·5861
4·0 „	0·6143
5·0 „	0·6185

From this, it is plain that the amount of precipitate is not much increased by great excess of the tungstate beyond a certain point. In the cold, precipitation is much less perfect, while, by boiling, fully three-fourths of the theoretical yield of oxide from the tartrate can be obtained.

By working with cold solutions a mixture may be made which remains clear long enough to permit polarimeter observations to be taken. I dissolved 5 grms. of the tartrate in 60 c.c. of water, cooled to 20°, and added five-tenths grm. of the tungstate in 20 c.c. of water. The mixture was made up quickly to 100 c.c. at 20° and polarised in the 200 m.m. tube immediately and after intervals of five minutes. I found without re-filling the tube:—

First observation α_D = 11·66°
Second „ 12·03°
Third „ 12·13°
Fourth „ 12·53°

The solution became now too turbid, from separation of a precipitate, for further tests. On standing some hours, the remainder of the solution in the flask cleared after subsidence of its precipitate. A portion of this examined gave—

$$\alpha_D = 12·74°.$$

Another portion of the same solution, heated and then cooled to 20°, gave the same. A new solution prepared in the same manner gave, after standing some time,—

$$\alpha_D = 13·11°.$$

I made next a solution containing in 100 c.c. 5 grms. of the tartrate and 1 grm. of the tungstate. This examined, immediately, at 20°, gave—

$$\alpha_D = 9·42°,$$

but it soon became turbid and deposited a precipitate. After clearing, I found—

$$\alpha_D = 11·48°,$$

which increased to 11·87° by heating the liquid.

These reactions are especially interesting when compared with those between the tartrates and other salts. We have here, as before, a marked decrease in the specific rotation on mixing the solutions of the active and inactive substances. But in the case of the tungstate, on standing, there is an increase instead of a decrease in the rotation observed in the other cases. This behaviour finds its explanation probably in the action of the liberated tungstic acid. The reaction between the two salts undoubtedly follows this equation:—

$$2KSbOC_4H_4O_6 + Na_2WO_4 = \\ = 2KNaC_4H_4O_6 + Sb_2O_3 + (WO_3)x.$$

The precipitation of the tungstic acid is very slow and incomplete. While in solution, it may combine with the soluble tartrate to form a body with increased rotation, the possibility of which is shown by the researches of Gernez and others. The delay in the appearance of the precipitate may be due to the formation and slow breaking up of intermediate products containing the antimony and tungstic oxides in temporarily soluble condition. With liberation of the tungstic acid we have a gradual increase in the already decreased rotation. This change in the rotation, before precipitation, is well shown in the following observations. I dissolved 5 grms. of the tartrate and 2 and five-tenths grms. of the tungstate, mixed at a low temperature and made up to 100 c.c. as before, and at exactly 20° C. A reading with the 200 m.m. tube was made as soon as possible, and, without changing the solution, this was repeated at frequent intervals. The results were as follows:—

3 hours 28 minutes α_D = 5·66°
„ = 5·96°
„ = 6·45°
„ = 6·83°
„ = 7·15°
„ = 7·32°
3 hours 44 minutes „ = 7·43°
3 hours 58 minutes „ = 7·90°

At this point the liquid began to grow slightly turbid, so that the observations could not be continued. The remainder of the liquid was then heated in a closed flask to complete the precipitation, cooled to 20°, and tested. I found now—

$$\alpha_D = 9·13°.$$

The liquid still remaining was filtered, 50 c.c. of the filtrate taken and precipitated with hydrogen sulphide, yielding finally 0·4045 grm. of antimony sulphide. From this it appears that, of the tartrate originally taken, 1·599 grms. remained in solution in the 100 c.c. (no allowance being made for the volume of the precipitate).

From this we have—

$KSbOC_4H_4O_6.\frac{1}{2}H_2O$	decomposed =	3·401 grms.
,, ,,	remaining	1·599 ,,
$KNaC_4H_4O_6.4H_2O$	formed	2·888 ,,

Now, the rotation corresponding to the tartar emetic remaining is 4·50°, and that to the Rochelle salt formed is 1·25°, from which we should expect a total rotation of 5·75°. This, in fact, corresponds very nearly to what was observed at the beginning of the test, and seems to bear out the suggestion made above: viz., that the principal reaction here occurs before actual precipitation appears. A splitting of the tartar emetic is indicated by the immediate decrease in the rotation, and then the complex effect of addition of the liberated tungstic acid to the alkali tartrate in solution appears from the gradually increased rotation. Precipitation finally follows as the end of the reaction; the separated part assumes the insoluble form.

It will be recognised that the phenomenon in this case is much more complex than in the other. There is nothing to show that while the rotation is being increased by the action of the tungstic acid there is not also a tendency toward decrease because of progressive decomposition of the potassium antimonyl tartrate. In all probability the observed rotation is a resultant effect.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1895.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Extraordinary General Meeting.—The following change in the Bye-laws was proposed from the Chair, and passed.

In Bye-law 1, the last paragraph, beginning "The life composition fee," was struck out and the following inserted:—

"The life composition fee shall be Thirty Pounds, excepting that Fellows who have paid ten annual subscriptions shall pay as life composition fee Twenty Pounds; Fellows who have paid fifteen annual subscriptions shall pay Fifteen Pounds; Fellows who have paid twenty annual subscriptions shall pay Twelve Pounds; and Fellows who have paid twenty-five annual subscriptions shall pay Ten Pounds."

At the ordinary Scientific Meeting which followed, Messrs. George J. Ward, John Wilson, E. S. Barralet, and W. A. Greaves, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Henry Farr, Uckfield; Edward Henry Grossman, 12, Alfred Place West, S.W.; C. E. Harrison, 53, Lansdowne Road, W.

The following were duly elected Fellows of the Society:—John Croysdale, Joseph Lones, James Morison, Arthur E. Potter, M.A. B.Sc., Edwin James Read, B.A., Albert Joseph Simons.

Of the following papers those marked * were read:—

*81. "*On the 'Isomaltose' of C. J. Lintner.*" By Horace T. Brown, F.R.S., and G. Harris Morris, Ph.D.

The paper gives a detailed account of the authors' investigations into the nature of Lintner's "isomaltose," and their results are summed up in the following conclusions:—

1. When the products of a starch-transformation by diastase are submitted to any known process of fractionation, the properties of each and every fraction strictly conform to the "law of definite relation" of opticity and reducing power.

2. The "isomaltose" of C. J. Lintner is not a chemical entity, but can be further split up by careful fractionation with alcohol and by fermentation, in such a manner as to indicate that it is a mixture of *maltose* and dextrinous substances of the malto-dextrin or amyloïn class. We must therefore cease to use this term "isomaltose" in relation to any of the products of the diastatic conversion of starch.

3. The crystallisable osazone which Lintner has described as "isomaltosazone," and upon which he has mainly founded his belief in the existence of "isomaltose," is nothing but "maltosazone" modified in its crystalline habit and melting-point by the presence of small but variable quantities of another substance.

4. The substance or substances which are capable of thus modifying maltosazone are the products of the action of phenylhydrazine on the dextrinous substances mentioned in 2.

5. This can be shown (1) *analytically*, by careful fractionation of the starch-products by alcohol, and also by fermentation; and (2) *synthetically*, by the re-crystallisation of pure maltosazone in the presence of the non-crystallisable products of the action of phenylhydrazine on the maltodextrins.

6. The only substance amongst the products of starch-transformation by diastase which is capable of yielding a crystallisable osazone, is *maltose.*

7. The results of the investigation bring out very clearly the danger of attempting to identify the carbohydrates in mixtures solely by the properties of their osazones, as these properties are liable to considerable modification by other substances of the same class which may not in themselves be crystallisable or readily separable from aqueous solutions.

Discussion.

Mr. Arthur R. Ling claimed priority on behalf of himself and Mr. J. L. Baker in having pointed out that Lintner's so-called isomaltose is not a homogeneous compound (*Proc. Chem. Soc.*, 1895, 3). In this communication they had also adduced strong evidence in favour of the view that the so-called isomaltose is a mixture of maltose and the simple dextrin, $C_{12}H_{20}O_{10}$, and they had proved that the osazone melting at 150—152° has the composition of a hexatriosazone.

82. "*Action of Diastase on Starch: Nature of Lintner's Isomaltose.*" By Arthur R. Ling and Julian L. Baker.

In a previous communication (*Proc. Chem. Soc.*, 1895, No. 146, 3) the authors have described the isolation of a substance from the transformation-products of starch by the diastase prepared from low-dried or green malt. This substance had approximately the optical and cupric reducing powers of Lintner's so-called isomaltose. Analyses and cryoscopic determinations made with this substance indicated that it had the molecular formula $C_{12}H_{22}O_{11}$; but the essential difference between it and the so-called isomaltose of Lintner was that it yielded maltosazone together with a very small quantity of an osazone melting at 145—152° on treatment with phenylhydrazine acetate, whereas Lintner states that his compound yields a single characteristic osazone melting at 150—152°. The authors have examined the low melting osazone obtained from their product, and conclude that it is merely impure maltosazone. More recent experiments carried out by the authors support their view that Lintner's so-called isomaltose consists of a mixture of maltose and the simple dextrin, $C_{12}H_{20}O_{10}$ (*loc. cit.*). No glucose is present among the products of the action of diastase from low-dried malt on starch, and diastase from this source is without action on maltose.

It was previously shown (*loc. cit.*) that when starch is transformed at 70° with the diastase prepared from kiln-dried or brewer's malt, the fraction which should correspond with Lintner's isomaltose gives, on treatment with phenylhydrazine acetate, glucosazone together with an osazone agreeing in crystalline appearance and melting-point with the so-called isomaltosazone of Lintner, but having the composition $C_{18}H_{30}O_{14}(N_2HPh)_2$, as if derived from a *hexatriose*, $C_{18}H_{32}O_{16}$. A diligent search has therefore been made for this triose among the transformation products last mentioned, but no crystalline compound has been isolated from them with the exception of maltose. Glucose was invariably present in small amount, and the authors find that when maltose is treated at 70° for two hours with the diastase prepared from high-dried malt, the presence of about 20 per cent of glucose is indicated by the increased cupric reducing power and the diminished optical activity; glucose was also detected qualitatively by the production of glucosazone. Bearing in mind the presence of glucose, as also their suggestion that Lintner's isomaltose contains the simple dextrin, it occurred to the authors that the triosazone was possibly produced by the interaction of this dextrin and glucose with phenylhydrazine; and this turns out to be the case. When the supposed isomaltose is treated with phenylhydrazine acetate in presence of glucose, the portion of the product soluble in hot water consists of a mixture of the triosazone and maltosazone.

*83. "*The Transformation of Ammonium Cyanate into Urea.*" By JAMES WALKER, D.Sc., Ph.D., and F. J. HAMBLY.

The transformation of ammonium cyanate into urea is reversible, about 5 per cent of urea in decinormal aqueous solution at 100° being re-transformed into ammonium cyanate. The direct transformation obeys the laws of a bimolecular reaction, and not of a unimolecular reaction, as might be expected. This is accounted for by the assumption that the ammonium cyanate is largely dissociated into ammonium ions and cyanic ions, and this assumption is confirmed by the influence of ammonium sulphate, potassium sulphate, potassium cyanate, and other substances, on the rate of the reaction. The dissociation theory also enables us to calculate the quantitative phenomena taking place when the transformation of urea into ammonium cyanate occurs in presence of silver nitrate. The speed of the reaction varies greatly with the temperature, and the variation may be expressed by means of van 't Hoff's formula.

*84. "*Note on the Transformation of Ammonium Cyanate into Urea.*" By H. J. H. FENTON, M.A.

Some years ago the author made a short communication to the Cambridge Philosophical Society upon this subject. ("The Metameric Transformation of Ammonium Cyanate," *Proc. Camb. Phil. Soc.*, 1888, 307.) Details of these experiments were not published, as it was intended to make further experiments. The reason for giving these details in the present note is that, in the list of papers to be read at the present meeting, there is one which has the above title, and it was thought that the observations might be of interest to the authors. Unfortunately the *Proceedings of the Cambridge Philosophical Society* are not often seen by chemists outside Cambridge, so that it is hardly to be expected that these authors should be aware of this communication.

In a previous paper (*Trans. Chem. Soc.*, 1878) I showed that urea when treated with sodium hypochlorite, in presence of caustic soda in the cold, evolves only one-half of its nitrogen in the free state, the remainder being retained in form of cyanate. The latter gives no nitrogen with hypochlorite or hypobromite.

Ammonium cyanate was prepared by direct union of cyanic acid vapour and dry ammonia. Weighed portions of this salt were acted upon by sodium hypobromite and hypochlorite, and excess of soda, with the following results:—

With sodium hypobromite—

I. 0·0544 grm. AmCyO gave 9·3 c.c. nitrogen (corr.).
II. 0·0562 ,, ,, ,, 9·93 ,, ,,

Since with hypobromite estimations, as conducted in the usual way, there is a deficiency of about 8 per cent in the nitrogen evolved, a correction for this was applied, giving (I.) 10·10 c.c., and (II.) 10·79 c.c. Theory for *half* the nitrogen requires 10·11 c.c. and 10·45 c.c. respectively.

With sodium hypochlorite—

	Theory for ½ N_2.
0·0620 grm. AmCyO gave 11·89 c.c. nitrogen (corr).	11·53
0·0692 ,, ,, 13·08 ,, ,,	12·87
0·0905 ,, ,, 16·34 ,, ,,	16·83

It is evident, therefore, that this salt evolves only half its nitrogen in the free free state with either reagent.

These facts obviously suggest a method by which it is possible to estimate the extent to which ammonium cyanate has been transformed into urea.

Let V = volume of nitrogen obtained by the action of hypobromite when a given weight of ammonium cyanate is taken and partly or entirely converted into urea; and let V_1 = total volume of nitrogen contained in the substance taken. Then the nitrogen due to the urea formed will be $2V - V_1$. For convenience the percentage transformation may be expressed as $2V - V_1/V_1 \times 100$.

Applying this method, the following results were obtained:—

0·7632 grm. AmCyO was dissolved in water and the solution made up to 100 c.c. 10 c.c. were taken for each experiment.

	Temp.	Time.	Vol. of N_2 (corr.)	Theory for ½ N_2.	Transformation.
I.	Ordinary (about 19°)	Immediate	14·14	14·19	None
II.	37°	18 hours	19·0	—	33·8
III.	37°	3 days	20·54	—	44·7

0·5561 grm. AmCyO dissolved in water and made up to 100 c.c. 10 c.c. taken.

I.	Ordinary	20 hours	12·60	10·34	20·3
II.	—	—	12·28	—	—
III.	100°	1 hour	17·57	—	69·9
IV.	100°	2½ hours	19·03	—	84·0
V.	100°	20 hours	19·50	—	88·5

0·9495 AmCyO in 100 c.c. 10 c.c. taken.

I.	70°	1 hour	25·9	17·66	46·6
II.	70°	4 hours	28·5	—	61·3
III.	70°	40 hours	30·4	—	72·1

In each case the liquid was measured into a small, partly drawn off test-tube, which was afterwards sealed. A correction for the loss of 8 per cent is made in the stated volumes of nitrogen.

These results indicate that the change proceeds rapidly at first, then becomes slower, and finally reaches a limit which is a function of the temperature. In no case examined was the transformation complete.

These facts suggest that the action may be a reversible one; urea and ammonium cyanate are perhaps tautomeric forms transformable one into the other. This hypothesis would account for some of the properties of urea which are otherwise difficult to understand. For example, the difference in the actions of hypobromite and hypochlorite (in presence of soda), mentioned above, might be explained in the following way:—The action of hypobromite is nearly instantaneous, whereas that of hypochlorite is extremely slow. The solution of urea may contain urea and ammonium cyanate in a state of equilibrium, the urea, of course, largely preponderating. Hypobromite therefore evolves nearly all the nitrogen—all from the urea, and half from the ammonium cyanate. Hypochlorite, however, it may be supposed, attacks only the ammonium cyanate, liberating half of its nitrogen, the other half remaining as cyanate which is not further decomposed. This would destroy the equilibrium of the system, and a further transformation of urea into ammonium cyanate would result. The latter would be removed as before, and finally one-half of the total nitrogen would be evolved in the free state,

There are indications also that cyanate is produced when urea solution, mixed with potash in excess, is left to stand for several weeks in a bell-jar over sulphuric acid. This fact could be explained in a similar manner.

*85. "*Some Derivatives of Humulene.*" By Alfred C. Chapman.

In a former communication (*Trans. Chem. Soc.*, 1895, lxvii., 54) the author described a sesquiterpene obtained from the essential oil of hops by fractional distillation, for which he suggested the name humulene. In that paper a nitrosochloride (m.p. 164—165°) was described, and also a nitrol-piperide obtained from it (m.p. 153°).

In the present paper the author gives an account of the following additional humulene derivatives:—

Hydrochloride of humulene nitrol-piperide—
$(C_{15}H_{24}NO{\cdot}NC_5H_{10}.HCl)$.
—This was obtained by passing dry hydrogen chloride into a solution of the nitrol-piperide in ether. The platinichloride of this salt crystallising from alcohol in reddish needles was also prepared (m.p. 187—189°).

Humulene nitrol-benzylamine—
$(C_{15}H_{24}NO{\cdot}NHCH_2C_6H_5)$.
—This compound was obtained by heating humulene nitrosochloride with an excess of benzylamine. After crystallisation from boiling alcohol it melted at 136°. The hydrochloride of this base was prepared by passing hydrogen chloride into an ethereal solution of the compound (m.p. 187—189°).

Humulene nitrosate $(C_{15}H_{22}N_2O_4)$.—Prepared by acting with nitric acid upon a mixture of humulene and amyl-nitrite in glacial acetic acid. It crystallises from benzene in small colourless needles, melting at 162—163°.

Humulene nitrosite $(C_{15}H_{24}N_2O_3)$. — This compound was prepared by allowing nitrous anhydride to combine with humulene dissolved in petroleum ether. After one re-crystallisation from boiling alcohol the compound was obtained in the form of magnificent deep blue needles, melting at about 120°). The mother-liquor from which this compound separated deposited colourless needles, which, after re-crystallisation, melted at 166—168°, and were found to be isomeric with the blue compound. This latter could be almost completely converted into the white substance by the long-continued boiling of its alcoholic solution.

*86. "*Note on Thio-derivatiaes from Sulphanilic Acid.*" By L. Edna Walter.

When diazotised sulphanilic acid and potassium xanthate are allowed to interact, following Leuckart's directions (*J. Pr. Chem.*, 1890, xli., 179), the parasulphonate-xanthate of the formula $SO_3K{\cdot}C_6H_4{\cdot}S{\cdot}CS{\cdot}OEt$ is readily formed as an easily soluble crystalline salt. On hydrolysis this xanthate undergoes change in two ways, and yields both the sulphydride, $SO_3K{\cdot}C_6H_4{\cdot}SH$, and the sulphethide, $SO_3K{\cdot}C_6H_4{\cdot}SEt$. As the former, however, is very readily oxidised, the corresponding disulphide is usually obtained. When acid is used in effecting hydrolysis, the disulphide is the only product; but when alkali is used the product is a mixture which apparently is the richer in sulphethide the more concentrated the alkali.

When the dried xanthate is heated at about 200° it loses considerably in weight, being converted into the sulphethide, which is more easily prepared in this way: only a small amount of disulphide is produced in this case.

The potassium disulphide crystallises in needles; it is very soluble in water, and sparingly soluble in alcohol. It yields a crystalline sulphochloride melting at 142°, and a sulphonamide melting at 253°.

The potassium sulphethide is very soluble in water and in alcohol; it crystallises in six-sided plates. The barium salt crystallises in very characteristic rhombic plates; its sulphochloride melts at 33°, and its sulphonamide at 134°.

The sulphethide is converted by oxidation with permanganate into the corresponding sulphonate, which is soluble in water, and yields a sulphochloride melting at 103·5°.

The sulphide, on the other hand, very readily yields benzeneparadisulphonate when oxidised by permanganate. The xanthate may also be directly converted into paradisulphonate by oxidation with permanganate, and it is easy in this manner to prepare any desired quantity of benzeneparadisulphonic acid.

One disulphochloride, $C_6H_4(SO_2Cl)_2$, prepared from the product, fuses at 136·5, several degrees higher than the melting-point assigned by Körner and Monselise.

*87. "*Helium, a Constituent of Certain Minerals.*" Part II. By William Ramsay, F.R.S., J. Norman Collie, Ph.D., and Morris Travers, B.Sc.

The first part of this communication contains an account of the sources of helium. About thirty minerals have been investigated, mainly those containing uranium, and of these fifteen contained helium in greater or less amount. Many, in addition, evolved hydrogen, a hydrocarbon, and carbon dioxide.

The second part treats of the densities of samples from different sources. After purification, the value 2·2 was obtained for three samples—one from clèveite, one from bröggerite heated alone, and one from bröggerite fused with hydrogen potassium sulphate. It was proved during these experiments that hydrogen is not evolved in combination with helium by the action of acid on mineral containing helium. The density of all these samples, united and carefully purified, was 2·218; a second purification made the density 2·228, practically an identical number.

The wave-length of sound in the gas corresponds accurately to the ratio $1 : 1\frac{2}{3}$, implying monatomicity, if that be granted to mercury on the same and on different grounds. The atomic weight would therefore be 4·4.

The solubility in water is 0·007 at 18°. Helium is therefore the least soluble of gases. It is insoluble in alcohol and in benzene.

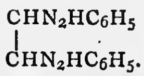
The paper concludes with a discussion of the relations of helium towards other elements.

88. "*New Formation of Glycollic Aldehyde.*" By H. J. H. Fenton, M.A.

The properties of the acid $C_4H_4O_6{\cdot}2H_2O$, which was described by the author in a previous paper (*Trans. Chem. Soc.*, 1894), are still being investigated with a view of establishing the constitutional formula for the acid. The present paper deals with the decomposition which the acid undergoes when heated with water. It is shown that, under these circumstances, glycollic aldehyde and carbon dioxide are produced, the change taking place almost quantitatively according to the equation—

$$C_4H_4O_6 = C_2H_4O_2 + 2CO_2.$$

The glycollic aldehyde was identified by oxidation to glycollic acid and by the action of excess of phenylhydrazine acetate, which gave the phenylosazone of glyoxal,—



$$\begin{array}{l} CHN_2HC_6H_5 \\ | \\ CHN_2HC_6H_5. \end{array}$$

This decomposition affords a very simple method for the preparation of glycollic aldehyde.

By spontaneous evaporation of the aqueous solution (and purification from a trace of glyoxylic acid produced) the aldehyde was obtained in an isolated condition as a viscid syrup, pure, except for a trace of ether or alcohol, which is obstinately retained. On removing this ether by heating under reduced pressure, the aldehyde undergoes polymerisation, a sweet-tasting solid gum being the result. Molecular weight determinations indicate that this substance is a form of hexose, $C_6H_{12}O_6$. It reduces Fehling's solution in the cold, and gives an osazone melting at 162—163°.

89. "*Ethereal Salts of Ethanetetracarboxylic Acid.*" By James Walker, Ph.D., D.Sc., and J. R. Appleyard.

Symmetrical dimethylic dihydrogen ethanetetracarboxylate should, according to stereochemical theory, exist in an inactive and a racemic modification, and the corresponding potassium salts should yield, on electrolysis, dimethylic maleate and dimethylic fumarate respectively. An attempt was made to separate the two modifications, but it was unsuccessful. The mixed dimethyl dipotassium salts, on electrolysis, gave a small quantity of dimethylic fumarate. The following derivatives of *ethanetetracarboxylic acid* were prepared in the investigation. *Tetramethylic salt*, m. p. 104°, symmetrical. *Dihydrogen dimethylic salt*, m. p. 158—160° with decomposition. *Triethylic monomethylic salt*, m. p. 58°. *Diethylic dimethylic salt*, liquid.

90. "*On the Occurrence of Argon in the Gases Enclosed in Rock Salt.* By P. Phillips Bedson, M.A., D.Sc., and Saville Shaw.

The brine obtained from the wells sunk in the rock salt deposit on the north bank of the Tees, in the neighbourhood of Middlesbrough, when pumped to the surface is found to be strongly effervescent. The gas, the liberation of which gives rise to this phenomenon, had been analysed by one of us some years ago (*J. Soc. Chem. Ind.*, 1888, 660 to 667), and found to consist of—

	By volume.
Methane	2·05
Nitrogen	97·95
	100·00

It was thought that a re-examination of this gas, with a view of testing its freedom or otherwise from argon, would be of interest. Through the kindness of Mr. Alfred Allhusen, a fresh sample was accordingly procured in May of the present year, when it was found to have slightly altered in composition and to contain—

	By volume.
Oxygen	1·3
Nitrogen	98·7
	100·0

only a minute quantity of methane being present, and the small amount of oxygen probably due to air leakage.

Professor Ramsay kindly furnished details of the simplest method for ascertaining the presence of argon in the gas—"sparking" over caustic soda in presence of oxygen, and submitting the residue after contraction ceased to spectroscopic examination. A small induction coil, giving a ¾-in. spark in air and actuated by the current from a battery of storage cells, was employed. About 40 c.c. of the gas was submitted to examination in each experiment. The sparking was continued in presence of an excess of oxygen until no further contraction was noticeable. After this it was found necessary to continue the sparking for an hour or two, until examined spectroscopically the nitrogen lines, which grew fainter and fainter, finally disappeared. After absorbing the excess of oxygen present with alkaline pyrogallate, the small residue was added to an already measured volume of pure oxygen, and the whole accurately measured, using the apparatus of Professor Dittmar in conjunction with a form of Lunge volumeter.

Two estimations gave results as follows:—

$$\left.\begin{array}{l}\text{I. } 1{\cdot}205\\ \text{II. } 1{\cdot}269\end{array}\right\}\text{Mean} = 1{\cdot}24 \text{ per cent of argon.}$$

The amount of argon present in the nitrogen from the rock salt is thus practically identical with the amount present in the nitrogen of ordinary air as determined by Lord Rayleigh and Professor Ramsay. This is to the authors' knowledge the first recorded analysis of a sample of naturally occurring nitrogen which has been stored up for some thousands of years under conditions which practically preclude the possibility of change. The nitrogen was probably in the first instance derived from the atmosphere, and it is of considerable interest to note that atmospheric nitrogen at the present day is still associated with the same percentage of argon as when in remote ages it was first occluded in cavities in the rock salt.

As Professor Ramsay has shown that argon is soluble to a considerable extent in water, it is proposed to examine the gas given off on boiling the brine after effervescence has subsided. In this way a gas would probably be obtained much richer in argon, and, as there would be little difficulty in procuring it in quantity, it might prove a useful source of the new gas. It is also proposed to submit the nitrogen found enclosed in coal to a similar examination.

91. "*On the Dissociation of Gold Chloride.*" By T. K. Rose, D.Sc., A.R.S.M.

The tensions of dissociation of trichloride of gold at various temperatures up to 332° were measured, the limited chemical action investigated being expressed by the equation—

$$AuCl_3 \rightleftharpoons AuCl + Cl_2.$$

The total pressures observed when a mixture of $AuCl_3$ and AuCl is heated in a closed space are higher than the tensions of dissociation, owing to the vapour-pressure of $AuCl_3$, which becomes considerable between 200° and 390°. The attainment of the maximum pressure is greatly delayed if the substances are carefully dried.

An investigation by means of Deville's "hot and cold tubes" showed that $AuCl_3$ undergoes continuous volatilisation in chlorine gas at atmospheric pressure at all temperatures between 180° and 1100°, the limits of temperature employed. The curve illustrating the rate of volatilsation under these conditions passes through a maximum at about 300°, and a minimum between 800° and 900°. Reasons for the shape of the curve are adduced.

The results afford evidence that Krüss's statements on the decomposition and volatilisation of gold chloride cannot be substantiated, but that those of Boyle and of Debray are in accordance with fact. It is pointed out that, according to the laws of chemical equilibrium, compounds formed with evolution of heat cannot be included in the class of bodies which are completely decomposed at moderate temperatures and again formed at much higher temperatures. The statements of Krüss regarding the behaviour of gold chloride at various temperatures, and those of Langer and V. Meyer regarding platinum chloride, are therefore at variance with theory, and in the former case have been shown to be unfounded.

(To be continued.)

NOTICES OF BOOKS.

Chemists and their Wonders. The Story of the Applications of Chemistry to various Arts and Manufactures. By F. M. Holmes. London: S. W. Partridge and Co. Crown 8vo., pp. 160.

The reader will find here a readable, bright, and most instructive survey of the services which chemistry is rendering to civilisation. It is drawn up in the form of a conversation between several interlocutors, one of whom, aptly spoken of as "Mr. Flippant," does not think much of chemistry until fairly beaten off the field. He pleads that "chemists don't build bridges or make railway trains!" We may here mention that there exists in the minds of County Councillors, &c., a delusion that chemists are inferior to engineers, and they even hand over to the latter work which can be done aright only by the former. Thus, when the manner of disposing of the sewage of London was under discussion, it was proposed that the task should be assigned to the engineer who had constructed the Tay Bridge!

Another school of unqualified censors accuse us of "imperfect drainage, of devising benumbing poisons, and contriving infernal machines." Whilst a third, though kindred, faction think that we might be good and happy without any knowledge of rare earths, or even if they had no existence. Our author does much to sweep such cobwebs out of the heads of all sensible people.

In his sketch on the rise of alchemy, however, he concedes too much to the old notion that this romantic delusion was the parent of chemistry. This question has been of late exhaustively discussed by the great French *savant* Berthelot. A little further Mr. Holmes touches on the peculiarly English error that chemistry is especially connected with drugs and medicines. This mistake is due to the unfortunate fact that in these realms the dealers in, and compounders of, medicines have contrived to appropriate the term "chemists" in place of their legitimate name, "pharmacists."

In the work we find an exposition of the most salient features of the lives and researches of Boyle, of Lavoisier, Chevreul, of John Young (of "paraffin" celebrity), of John Walker, of Scheele, of W. Murdoch (the gas manufacturer), with his predecessors, Shirley and Clayton, the latter dating back to 1739. Winzer, or Winsor as he renamed himself, receives mention, and though he did not invent gas, was the inventor of gas companies—a blessing for which chemical science can scarcely be held responsible.

The expression here used of "enriching" coal-gas with both oil-gas and water-gas is misleading. Water-gas, sometimes spoken of as "Dowson gas," enriches coal-gas chiefly in the deadly product carbon monoxide. A speaker here doubts whether it would answer well in England if used alone. The reason is because our sanitary laws are more stringent than those of the United States.

"High" explosives receive a very full notice. As a set-off to the fearful dangers consequent upon any oversight or irregularity in their manufacture and use, it is here pointed out that the dynamitards and anarchists are liable to fail from the difficulty of manufacturing a safe article without an amount of care not easily secured when the process is carried on illegally. It is, however, to be again remembered that the dangers of ill-made dynamite do not always fall upon the guilty parties. It may be asked whether the economy of time and labour from the use of the high explosives in place of gunpowder, is a sufficient compensation for the destruction of life and property attending upon their employment.

Other ably-written and luminous chapters treat of the coal-tar colours, of photography, of indiarubber and its transformations, of chemical manures, of aërated water, and of disinfectants and germicides.

Few of the outside public, even of the so-called "intelligent and respectable classes," can read these chapters without having their eyes opened, literally and, even still more, figuratively. It might, of course, have been briefly pointed out that our disgraceful inferiority in the manufacture of the coal-tar colours is due to the joint action of two causes: the fact that our students instead of being trained in discovery, are compelled to waste their time and energies in "preparing for exams."; and, secondly, to the laxity of our laws, which allow an alien to hold a British patent without attempting or intending to put it in use on British soil.

The work before us merits the warmest recommendation.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 25, June 24, 1895.

Further Studies on the Fluorescence of Argon and on its Combination with the Elements of Benzene.—M. Berthelot.—(See p. 13).

On the Lactones or Campholenic Olides.—MM. Berthelot and Rivals.—It results from the author's researches that the lactones have formation-heats notably superior to those of the isomeric acids; the deviation measured between the liquid acid and the inactive lactone being $143{\cdot}8 - 131{\cdot}7 = +12{\cdot}1$.

Solution of Neutralisation Heats of the Campholenic Acids.—M. Berthelot.—The author has determined the heats of the liquid and solid campholenic acid and of campholic acid.

Reduction of Silica by Charcoal.—Henri Moissan.—M. Moissan has obtained a very decided reduction by heating a mixture of rock-crystal and of carbon in powder in a cylinder of coke closed at one end. If the temperature is not very high a part of the silicon escapes the action of the carbon, and is found in the state of crystals or of fused globules. This procedure may be applied to the preparation of silicon by refrigerating its vapour at the moment of production.

Condensation-products of Valeric Aldehyd (Methyl 2-Butanal-4). Observations concerning the Paper of Barbier and Bouveault.—C. Friedel.—The author has been for some time engaged with a study of the condensation-products of valeric aldehyd by the action of dilute soda, aqueous or alcoholic. One of these products is the substance which Barbier and Bouveault regard as dimethyl-26-heptene-3-methylal-3, and which they have further condensed with acetone.

Properties of Solid Carbonic Acid.—P. Villard and R. Jarry.—Dry carbonic acid was distilled and solidified in a wide refrigerated tube in which a thermometer had been introduced axially. The melting-point of the solid acid was −56·7°. The pressure at the time was 5·1 atmospheres. The point of refrigeration was then observed and found to be −56·7° at the pressure of 5·1 atmospheres. This result agrees substantially with the figures found by Faraday. The point of ebullition of solid carbonic acid is at −79°. Regnault found −78·16 and Pouillet −79°. Ether mixed with solidified carbonic acid (carbonic snow) does not reduce the temperature. Methyl chloride behaves quite differently: setting out from −65° the carbonic snow dissolves without liberation of gas, and at the moment of complete saturation the thermometer marks −85°. The lowest temperature reached by means of carbonic snow *in vacuo* is −115°, a point which was maintained for nearly three hours.

On a Formula of M. Guye.—A. Colson.—Referring to a paper by Guye and Jordan (*Comptes Rendus*, p. 1274) the author holds that the simplified formula of Guye is unfounded, and that the direction of the rotatory power is not indicated in a satisfactory manner by a formula founded solely upon chemical hypotheses.

On the Alcohols Derived from a Dextro-Terebenthene, Eucalyptene.—G. Bouchardat and Tardy.—An attentive study of the derivatives of the various natural terebenthenes with different rotatory powers will probably enable it to be established that these carbides are merely mixtures of two active turpentines, dextro- and lævo-rotatory, meeting each other in variable proportions.

Condensation of the Non-saturated Aldehyds of the Fatty Series with Dimethylacetone; Synthesis of Aromatic Hydrocarbons.—Ph. Barbier and L. Bouveault.—The authors consider the condensation of methylethylacroleine with acetone and the condensation of α-isopropyl-β-isobutylacroleine with dimethylketone.

Double Combinations of the Nitriles belonging to the Fatty Series and to the Aromatic Series with Aluminium Chloride.—G. Perier.—This memoir is not adapted for useful abridgment.

Action of Air upon the Must of Grapes.—V. Martinand.—Of all the elements of must the red soluble colouring matter is the most readily oxidisable. In grapes of the type of the Petit-Bouschet there exists a colouring matter oxidisible by air, and one which is less so or not at all, and which does not hinder the action of the air from proceeding upon the other elements of the must. The bouquet of wine is due not only to the bouquets which exist pre-formed in the grape and to those developed during the fermentation, but also, in some varieties, to the elements contained in the must. The colouration of white wines and their taste are due to an oxidation of the must, and are not derived from fermentation. It is possible to prepare white wines with black grapes by extracting the total juice which they can yield, and submitting it, before fermentation, to the following operations:—Refrigeration to check fermentation, aëration to precipitate the colouring matter, and, lastly, filtration of the liquid to prevent its re-colouration during fermentation.

Treatment of the Bites of Venomous Serpents by Chloride of Lime and by Anti-venomous Serum.—A. Calmette.—MM. Phisalix and Bertrand erroneously ascribe to the author a view which he repudiates, *i. e.*, that chloride of lime has a vaccinal action. Conclusive experiments with chloride of lime have been made successfully upon human subjects, especially by Prof. Halford, at Melbourne. He is now sending out immunising serum in considerable quantities to India, the Antilles, and Australia. It is sufficient to inject into rabbits a dose of the serum equal to 1-10,000th of their weight to enable them to bear afterwards, without danger, a dose of venom capable of killing check specimens in from three to four hours.

MISCELLANEOUS.

Institute of Chemistry.—The following Candidates have passed the Examinations for Membership, July 2nd to July 5th, 1895:—*For the Fellowship*: Fuerst, Alexander Frankenbacher (Ph.D., Heidelberg), The University of Heidelberg. *For the Associateship* (under Regulations in force prior to October 1st, 1893): Andrews, Ernest Robert, Finsbury Technical College; Barnes, Charles Kepler, University College, Liverpool; Bodey, Augustus Charles, University College, Bristol, and Pharmaceutical Society's Research Laboratory; Bowie, James Girdwood, Mason College, Birmingham; Bowles, Horace Edgar, Finsbury Technical College; Buchanan, John, Glasgow and West of Scotland Technical College; Burbridge, James Kerry, King's College, London; Desch, Cecil Henry, Finsbury Technical College; Dodd, Frederick Robertson, Glasgow and West of Scotland Technical College, and Registered Student under A. Smetham, Esquire, F.I.C.; Guthrie, Thomas, Yorkshire College, Leeds; Hill, Charles Alexander, Pharmaceutical Society's Research Laboratory, and King's College, London (Physics); Hirst, Henry Reginald, Yorkshire College, Leeds; King, Herbert, Yorkshire College, Leeds; Meggitt, Loxley, University College, Nottingham; Ridding, Howard Charles (Assoc. R.S.M.), Royal College of Science, London; Warden, John Blair, Glasgow and West of Scotland Technical College, and School of Mines, Freiburg; Wharton, Frederick Malcolm, Mason College, Birmingham; Woollatt, George Henry, University College, Nottingham, and Royal College of Science, London. *Final Examination for the Associateship* (New Regulations): Robins, Walter (B.Sc. Lond.), Finsbury Technical College.

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.

Wanted, a Respirator.—Can any reader supply the name of maker of a respirator suitable for wear in the laboratory? Protection is desired against entrance of hydric sulphide into the lungs either by mouth or nose.—Asphyxia.

THE CHEMICAL NEWS.

Vol. LXXII., No. 1862.

A POSSIBLE COMPOUND OF ARGON.

By WILLIAM RAMSAY, F.R.S.

There are three ways of forming an endothermic compound. First, by choosing such a reaction as shall on the whole give rise to heat-evolution; as when potassium hypochlorite is produced by passing chlorine into a solution of caustic potash; water and potassium chloride are produced simultaneously with great heat-evolution, so that the algebraical sum of heat is positive. A second method is to use the silent discharge; and by this means oxygen can be oxidised into ozone. A third method depends on the fact that an endothermic compound is more stable at high than at low temperatures, and that if it can be suddenly withdrawn from a hot region a certain proportion, at least, will escape decomposition. By this means acetylene can be produced by causing an arc to play in an atmosphere of hydrogen.

The first of these methods would appear to be impossible with argon. No definite compound is known; much less one produced with heat-evolution.

The second method has been used apparently with some success by M. Berthelot.

The third method has recently been tried; and though much remains to be done, circumstances render it desirable that I should record in a preliminary note certain results which I have recently obtained.

The arc was made *in vacuo* between two thin carbon rods, enclosed in a globular bulb; this was in order to expel, to a certain extent at least, occluded gas. The bulb was then filled with argon, and placed in communication with a graduated reservoir of dry argon. After some four hours, in which the pressure was always somewhat above that of the atmosphere, so that leakage inwards could not have occurred, all was allowed to cool. The volume of the gas had *increased* by about one-fifth. No alteration of volume was caused in this gas on exposure to water, to caustic soda, or to ammoniacal cuprous chloride; hence the gas contained no carbonic anhydride or oxide. The spectrum of this gas, while showing a faint argon spectrum, exhibited a very finely channelled spectrum, so luminous as to give the impression of a continuous spectrum, together with certain lines which are not coincident with argon lines, judging by a careful comparison in which both spectra were in the same field. Mr. Crookes has kindly undertaken to examine the spectrum, and will doubtless report on it.

Further experiments will be made; but I must content myself at present with chronicling the few facts which I have observed.

University College, Gower Street,
July 26, 1895.

OPENING UP SILICATES BY MEANS OF PURE LEAD CARBONATE.

By P. JANNASCH.

The first chemist who made a successful attempt to decompose silicates quantitatively by fusion with lead oxide was G. Bong (*Zeit. f. Anal. Chemie*, xviii., p. 270). Subsequently W. Hempel and R. F. Koch (*Ibid.*, xx., p. 496) gave the preference to bismuth oxide. Recently I had the opportunity to experience the advantages of the use of lead oxide when effecting the analysis of some specimens of topaz in concert with H. Jas. Locke. The many experiments which I have lately made on incinerating and weighing lead- and bismuth-oxides in platinum vessels, induced me to attempt the opening up of silicates by direct mixture with pure lead carbonate and subsequent fusion in a platinum crucible. From these very successful experiments there originated the following general procedure for the analysis of silicates.

The requisite chemically pure lead carbonate is suitably obtained by precipitating a hot solution of lead acetate with the calculated quantity of ammonium carbonate.

The granular precipitate obtained is first washed in a tall beaker by repeated decantation, then distributed on several rapid filters (made by Desaga, of Heidelberg) *not folded filters*, perfectly washed with boiling waters, finally with suction, carefully removed from the paper without injuring it, and finally completely dried in a capacious porcelain capsule at the heat of the water-bath and with stirring.

For opening up silicates I use a large thick-sided platinum crucible, of 52 to 53 m.m. in height, 45 m.m. in width at the top, and weighing, together with its cover, 72 grms. We thus obtain better melts, and most completely avoid the volatilisation of traces of alkali.

For effecting the fusion we put into the crucible from ten to twelve times the quantity of dry lead carbonate, add the very finely pulverised and air-dried specimen (which has been weighed in a small tube), and mix thoroughly with the glass rod, and heat the whole—under cover, at first gradually, approaching the crucible with a flame of an inch in height for about fifteen to twenty minutes, whereby the greater part of the carbonic acid escapes; it is then more strongly heated to fusion at redness, but only about one-third of the height of the crucible must be actually red-hot. It is remarked that if the silicate contains organic matter, this must be first destroyed by gentle ignition before admixture with lead carbonate. It is also stated that the platinum crucible is less attacked than by a fusion with sodium carbonate or an alkaline hydrosulphate.

Care must be taken to use a thoroughly non-luminous flame, so as completely to obviate any action of reductive gases upon the contents of the crucible. After fusion for ten to fifteen minutes the crucible, when as glowing hot as possible, is plunged into cold distilled water, displacing the cover of the crucible by the tongs as little as possible. To prevent the projection of any small particles of the melt, with the aid of tapping the bottom of the crucible and gentle pressure of the sides, the cake of melt is caused to fall into a large flat Berlin capsule, corresponding quantities of pure concentrated nitric acid and hot water are added, and the whole is evaporated down on the water-bath, continually comminuting all the fragments of the melt as they are gradually disintegrated add softened, until there remain at last more or fewer light-coloured flocks of silica floating in the liquid. In the meantime the residue of the melt, which forms only a slight coating in the crucible, is placed, along with water and some strong nitric acid, in a boiling water-bath, and after a short time the solution obtained, including some silica, can be mixed with the chief quantity. The saline mass, after being sharply dried on the water-bath, is again moistened with at least 20 to 25 c.c. of concentrated nitric acid, and again evaporated down until as dry as dust. This residue when cold is moistened with 10 c.c. concentrated nitric acid, allowed to stand at rest for ten minutes, and then mixed with from 750 to 1000 c.c. of water, heated for fifteen minutes on the water-bath, and filtered from the silica, which is finally most carefully washed with boiling water, to which at first a little nitric acid is added.

The filtrate from the silica is mixed in the cold with a large excess of concentrated hydrochloric acid, in order to separate the bulk of the lead as a chloride, which, after subsidence, is then filtered with suction and washed with cold hydrochloric acid (1 vol. concentrated acid and 1 vol. water). This filtrate is again evaporated to dryness in a capacious capsule, especially for the complete expulsion of any free nitric acid. The residue is mixed with 30 c.c. dilute hydrochloric acid (1 : 4), and as much water heated on the water-bath for fifteen minutes and allowed to cool, when any residual traces of lead chloride are collected upon a very permeable filter, and quickly washed with cold water. The resulting filtrate now contains unimportant quantities of lead, which are finally quantitatively precipitated with hydrogen sulphide. To this end the gas is first introduced in the cold; it is then heated for some time until the lead sulphide has settled, and the liquid is finally allowed to cool in a current of sulphuretted hydrogen.

The precipitate, which is generally slight, is filtered off and washed with warm water, to which fresh sulphuretted hydrogen water is constantly added. Above all, care must be taken that the precipitation of the lead is really complete, as otherwise the further course of the analysis will be disturbed in the most troublesome manner, or inaccurate results will be obtained.

Then from the filtrate free from lead all hydrogen sulphide must be removed, by concentrating the solution before the iron is oxidised, by means of nitric acid or hydrogen peroxide, on undertaking the general procedure for separating iron, alumina, manganese, lime, magnesia, potash, and soda.

I have already had several analyses of rocks executed by a number of my pupils according to the above method, which agreed in their results most satisfactorily with the combined results of sodium carbonate fusion and opening up with hydrofluoric acid.

After further elaboration of the lead oxide method for the case of the simultaneous presence of titanium and phosphoric acid, I propose communicating all the analytical material in connection. I cannot sufficiently extol the use of lead carbonate in the analysis of silicates. As compared with the former methods, it means a very considerable economy of time, and it need fear no comparison with them as regards the accuracy of the results.—*Zeit. Anorgan. Chemie*, viii., p. 364.

NOVEL REACTIONS OF MORPHIA.

By G. BRUYLANTS.

On heating morphia or one of its salts in a steam-bath with a little pure concentrated sulphuric acid, and adding a drop of Fröhde-Buckingham reagent (1 c.grm. molybdate to 1 c.c. of acid), there is produced a splendid green colour, which lasts for some time and then disappears.

This reaction is almost as sensitive as the Fröhde reaction properly so called. It seems to me to have some importance, because we see the same reagent produce two distinct reactions with the same substance placed in different conditions, and also because this green colouration is characteristic of other alkaloids of opium.

To produce it we heat, for two or three minutes, the watch-glass on which we have placed the morphia and the sulphuric acid, then spread out a drop of the mixture on a plate of white porcelain, and add a drop of the reagent.

We may combine the lilac reaction of Fröhde, the green colouration and the reaction of Huseman, when operating on the same product. To this end we dissolve the morphia on a watch-glass in one or two drops of sulphuric acid. We spread out a part on the porcelain, and add an equal quantity of Fröhde's reagent, obtaining thus the lilac colour. Then we heat the watch-glass in the steam-bath, take a fresh portion of the mixture, and with a further quantity of the reagent we obtain the green colouration. Having observed this, we introduce into the liquid while still green a grain of nitre, when we immediately see the green tint give place to a red colour, which grows paler in time, and lastly turns yellow.

I take this opportunity to remark that it has been erroneously recommended to heat the mixture of morphia and sulphuric acid in the steam-bath for half an hour, to obtain Huseman's reaction; one or two minutes will be sufficient. Whatever may be the purity of the acid and the morphia, there always is produced, after heating for half an hour, a violet colour more or less intense,—a colouration which, in fact, has no influence upon the ulterior reaction with nitre when it is required to identify pure morphia. But it is no longer the same case if the morphia has been extracted from some part of a dead body in the course of a toxicological investigation. It is then always more or less contaminated with foreign matters which sometimes colour the test-liquid in a very intense manner, so that it becomes very difficult to seize upon the play of colours produced by the nitre.

If we heat the product only for one minute or two minutes, the mixture is very slightly coloured, and is very suitable for the reaction.

I arrange below, in a table, the colours produced by morphia and some of the other bases of opium, by the action of Fröhde's reagent on a solution of morphia in sulphuric acid before and after being heated in the steam-bath, as well as the colours produced by the addition of nitre to the product of the last operation.

Kind of Alkaloid.	I. Fröhde's Reagent on the Sulphuric Solution *before* heating.	II. Fröhde's Reagent on the Sulphuric Solution *after* heating.	III. As in II., followed by the addition of a grain of Nitre.
Morphia	Lilac colour.	Green colour.	Green colour, changes to red, which fades and disappears.
Apomorphia	Green-blue.	Do.	Do.
Oxidomorphia	Blue.	Do.	Violet, turning to red.
Codeia	Dirty green, then blue.	Do.	As morphia.
Narceia	Brown, turning to green and then to blue.	Dirty green.	Do.
Narcotina	Green, then greenish-brown.	Green.	Violet, then a fugitive red.
Papaveria	Green, then blue and then red.	Green, then blue and red.	Green colour, disappears at once.
Meconia	Green, very fugitive.	Greenish blue.	Do.
Cryptopia	Dirty green, then brownish-green.	Dark green.	Do.

II. It is known that, on adding an aqueous solution of iodic acid to a solution of morphia in sulphuric acid, there is produced a deposit of iodine. On adding iodic acid to the sulphuric solution of morphia previously heated in the steam-bath, we obtain, according to the proportions, a lilac which turns slowly to red and then disappears, or else a red at once. The former result is with a trace of iodic acid, the second is with a large proportion of that reagent. This character has some importance. — *Bulletin de la Soc. Chimique*, Series 3, xiii.-xiv., No. 9, p. 498.

ATOMIC WEIGHTS OF NICKEL AND COBALT.

By CLEMENS WINKLER.

The author has undertaken a revision of the atomic weights of nickel and cobalt, with the object of ascertaining which of the two has the higher atomic weight.

The experiments were effected by treating the metals with a solution of auro-potassium bromide, dissolving the metals in hydrochloric acid, determining the hydrogen evolved, treatment with solution of iodine in excess, and titrating back the excess of iodine.

The average of the determinations showed, for nickel, the value 58·7155; and for cobalt, 59·3678.

The author thinks that these figures must be accepted as the true atomic weights of nickel and cobalt, referred to H = 1 and I = 126·53.—*Zeit. Anorg. Chemie* and *Chem. Zeitung.*

RECENT ANALYSES OF LEUCITE BASALT FROM VESUVIUS.

By ALBERT THORPE.

I HAVE recently analysed samples of leucite basalt from Vesuvius, and the following results may be of interest to the readers of the CHEMICAL NEWS, as Vesuvius is now in a state of eruption.

	I.	II.
Silica	47·23	47·32
Alumina	18·23	18·00
Ferric oxide	4·21	4·23
Ferrous oxide	4·49	4·31
Manganous oxide ..	1·36	1·42
Lime	8·63	8·51
Magnesia	4·68	5·03
Potash	8·00	7·92
Soda	2·63	2·70
Titanic acid	0·23	0·36
Phosphoric acid ..	0·31	0·20
	100·00	100·00

The specific gravities of the basalt varied from 2·653 to 2·721.

ON CERTAIN PHENOMENA OBSERVED IN THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF POTASSIUM ANTIMONYL TARTRATE.*

By J. H. LONG.

(Concluded from p. 45).

Reaction with Sodium Thiosulphate.

COLD dilute solutions of the thiosulphate and potassium antimonyl tartrate can be mixed without immediate precipitation. Application of heat, however, produces a light yellow precipitate, which grows deeper and finally becomes bright red. This precipitate is the substance commonly known as antimony cinnabar, used as a pigment, and on the large scale is made by decomposing the thiosulphate by antimony chloride. In the reaction between the thiosulphate and tartar emetic the precipitate appears very heavy, but the decomposition is far from complete, as shown by the figures given below.

There seems to be some doubt as to the composition of this precipitate. Roscoe and Schorlemmer (ii., Part 2, 324) give it as, probably, SbS_2O; referring, however, to other formulæ. Dammer's "Handbuch" gives—

$$Sb_2O_3.Sb_2S_3$$

as the probable formula. Others are also given. Recently, Baubigny (*Comptes Rendus*, No. 17, 1894) has given reasons why the formula Sb_2S_3 should be considered the correct one, and the proof he presents appears to be satisfactory. There remains a possibility, however, that the composition may, under certain circumstances, vary with the method of preparation. In fact, some of my own results seem to show this, and I am now engaged in studying the question further. But, as made in the reaction in hand, the composition seems to be $2Sb_2S_3.H_2O$. This was determined by the following considerations:—The precipitate dissolves in hydrochloric acid without liberation of sulphur, yielding a perfectly clear solution. A solution made in this way was heated, mixed with a little tartaric acid solution, and precipitated by hydrogen sulphide in the usual manner. On filtering off the orange-yellow precipitate so obtained in a Gooch crucible, drying at 120°, and weighing, the weight was always found less than that of the antimony cinnabar taken.

Sulphur determinations were made by dissolving a grm. or less of the substance in strong S-free solution of potassium hydroxide, and then oxidising the sulpho-salt formed by washed chlorine gas (method of Rivot). The results of these tests were as follows:—

	Calculated for $2Sb_2S_3.H_2O$.	Found.
Sb	69·56	69·80
S	27·83	27·72

No determination of the water was made, but its presence was shown in the substance dried at 120° by heating to a higher temperature in a narrow glass tube.

In a series of experiments on the precipitation a number of portions of the tartrate, of 5 grms. each, were weighed out and dissolved in 150 c.c. of water. Varying amounts of the thiosulphate in 50 c.c. of water were added, and then water enough to make exactly 250 c.c. The flasks holding the mixtures were closed with perforated stoppers containing long glass tubes, and then heated in the water-bath one hour. In this way evaporation was practically avoided. At the end of the hour the precipitates were collected on a Gooch funnel, dried at 120°, and weighed with the following results:—

No. of experiment.	Weight of $Na_2S_2O_3 5H_2O$ added. Grms.	Weight of precipitate. Grm.
1.	0·1	0·0039
2.	0·2	0·0068
3.	0·4	0·0111
4.	0·8	0·0178
5.	1·6	0·0363
6.	3·2	0·0803
7.	6·4	0·2112
8.	12·8	0·4809

In a second set of tests I dissolved, in each case, 10 grms. of the tartar emetic in 100 c.c. of hot water and added the thiosulphate in 50 c.c. of hot water. The mixtures were kept at 100° two hours and then filtered. Results as follows:—

No. of experiment.	Weight of $Na_2S_2O_3.5H_2O$ added. Grms.	Weight of precipitate.
9.	5	0·1915
10.	10	0·4041
11.	15	0·5162
12.	20	0·6818

It is evident from these figures that in both sets of experiments the reaction is far from complete and not easily determined. It is, perhaps, quite complex. I noticed in no case the escape of hydrogen sulphide or sulphurous oxide, and the gradual change in colour during precipitation from very light yellow to bright red suggests that it takes place in two stages. Vortmann (*Ber. d. Chem. Ges.*, xxii., 2307) has studied the general problem of decomposition of thiosulphuric acid, and states that it breaks up into H_2S, O, and SO_2. In presence of certain metals, tetra- and pentathionates seem to be formed. It is certain that no sulphate is formed in the reaction in hand, but the proof of formation of the several thionic acids is difficult because of the incompleteness of the reaction and the presence of the great excess of thiosul-

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* *Journal of the American Chemical Society*, vol. xvii., No. 2.

phate. In cases of complete reaction, however, Vortmann and Vaubel, also (*Ber. d. Chem. Ges.*, xxii., 2703), have shown that these acids are formed.

I suggest, therefore, this explanation of the present reaction. At the outset there may be, as with borax, a decomposition according to this equation—

$$2KSbOC_4H_4O_6+Na_2S_2O_3+H_2O= \\ =Sb_2O_3+2KNaC_4H_4O_6+H_2S_2O_3$$

then—

$$Sb_2O_3+2H_2S_2O_3=Sb_2S_3+2H_2O+SO_2+O_5,$$

the oxygen and sulphur dioxide being held, however, to form polythionates.

The gradual change of colour can be accounted for by the gradual change of oxide into sulphide of antimony, and it seems possible that under certain conditions of concentration and temperature a part of the oxide should remain unchanged, accounting for the results of some of the analysts who have examined the precipitate. In several instances I modified the experiment by mixing warm solutions of the tartar emetic with warm thiosulphate solutions, and then throwing the mixture into a large volume of cold water the instant a precipitate began to form, to check the reaction. The precipitate which now settled was very light coloured instead of red, and appeared to be a mixture of oxide and sulphide. The microscopic appearance of this precipitate is distinctly different from that of the antimony cinnabar.

As explained at the outset, some time elapses after mixing cold solutions before a precipitate appears. In the beginning of the interval the solution may be so clear that accurate polarimetric observations are possible. But, contrary to expectations, based on the behaviour in other cases recorded, I find the specific rotation of the tartar emetic, in this stage of the reaction, quite unchanged. After precipitation a marked decrease was observed as usual. This is shown in the following table in which the filtrates from the last precipitates referred to were made made up to 250 c.c. before polarisation :—

No. of experiment.	Thiosulphate added. Grms.	α_D observed.	α_D calculated.
9.	5	10·90°	10·89°
10.	10	10·43°	10·46°
11.	15	10·07°	10·24°
12.	20	9·69°	9·93°

In the last column the rotations were calculated on the assumption that antimony is precipitated and Rochelle salt formed according to the last equations. In the eleventh and twelfth experiments the thiosulphate is present in amount much in excess of that necessary to complete precipitation by these reactions, and it is evident that a decomposition of the active molecule has taken place not indicated by the amount of precipitate.

There seems to be a fundamental difference between the reaction with the thiosulphate on the one hand, and those with the borate, carbonate, phosphate, acetate, and tungstate on the other. In the first case we appear to have no breaking up of the complex tartrate until actual precipitation occurs, while in the others the stages are quite distinct. I have shown that in these last reactions acids are liberated which may be readily recognised. It is also true that these acids are practically without action on antimonous oxide, from which it would follow that this substance might remain a long time, possibly in the hydrated form, in contact with the liberated acids without change. This would not be the case with liberated thiosulphuric acid. If set free in the presence of antimonous oxide, even the dry precipitate, it soon converts it into sulphide. Any cause, therefore, which acts to destroy the equilibrium in the solution of tartrate and thiosulphate must lead to the almost immediate formation of a precipitate.

In many of our most familiar cases of precipitation the formation of the precipitate is so rapid that we are accustomed to look upon it as instantaneous. But by varying the conditions of precipitation it may be shown that even the reaction between barium chloride and sulphuric acid is one which consumes an appreciable interval. In such cases, however, we have no means of knowing what takes place before the precipitate becomes actually visible. It is, doubtless, true that the liquid regarded as supersaturated for $BaSO_4$ does not begin to throw this out in solid form until a relatively large number of these molecules combine to produce a particle of a certain size, but at what rate the Ba and SO_4 ions combine cannot be shown.

But in the cases before us we have evidence, first, of the gradual breaking up of the complex potassium antimonyl tartrate, and then, also, that a relatively large amount of the antimony may be separated before any of it falls as a precipitate. The stage of precipitation seems to follow as a perfectly distinct and also progressive one. It is hastened, as in other cases of supersaturation, by heat or agitation. One of the reactions shows, also, that a relatively long time is consumed in combination as well as in dissociation. In the case of the mixture containing the tartrate and tungstate we have evidence of the splitting of the first molecule, and then, from the slowly increasing rotation, evidence of the addition of an element from the second to the active part of the first. Both of these phenomena are observed before precipitation appears.

It must be remembered that the several acids shown to be liberated in these experiments are all so-called weak acids, or acids but slightly dissociated in solutions. It is also true, as a test of their electric conductivities shows, that the solutions of tartar emetic are relatively little dissociated (see in this connection Hugo Haedrich, *Zeit. Phys. Chem.*, xii., 496). There is doubtless, therefore, a close connection between the phenomena outlined above, and others depending on the degree of dissociation of the ions in solution. A study of the behaviour of weaker solutions would doubtless lead to interesting results not brought out in the above experiments which were undertaken mainly to show the character and amount of precipitates formed. A discussion of the behaviour of dilute solutions will follow.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

First Paper : The Analysis of Strontic Bromide.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 43).

The Ratio of Silver to Strontic Bromide.

First Series.—In this series a slight excess of silver was taken, dissolved, and diluted with at least a hundred times its weight of water, and added to the strontic bromide in glass-stoppered flask. After the usual long-continued shaking, the precipitate was collected upon a Gooch crucible, and the excess of silver in the evaporated filtrate and first five or six wash waters was determined after Volhard's method (*Proc. Amer. Acad.*, xxix., 66). Upon subtracting this small excess of silver from the total, the amount corresponding to the strontic bromide remains. This method is not a very satisfactory one, the final result being probably too low, because of loss of a portion of the slight excess of silver.

Second Series.—Here the end point of the reaction was determined by titration after the method of Abrahall (*Proc. Amer. Acad.*, xxviii., 24), very weak solutions of silver and hydrobromic acid being used to titrate backwards and forwards. The mean reading was taken in each case, and the method of procedure resembled exactly the work with barium. These results are much more trust-

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* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy.*

worthy than the last. In several cases the sample of strontic bromide was first analysed by this method, and subsequently an excess of silver nitrate was added and the preceding method was applied.

Third Series.—For this series a new method was devised. According to Stas (*Mém. de l'Acad. Belg.*, xliii., Part ii., Introduction), argentic bromide is wholly insoluble in water; according to Goodwin (*Zeit. f. Phys. Chem.*, xiii., 645), it is only very slightly soluble; while according to Kohlrausch and Rose (*Zeit. f. Phys. Chem.*, xii., 234), it is soluble to the extent of three-tenths of a milligramme in a litre. The time during which chloride of silver is shaken makes an enormous difference in the solubility, and it is not impossible that a similar effect may occur here. Perhaps Kohlrausch and Rose did not agitate their precipitate so thoroughly as Stas did. According to the present experience the purest silver bromide was capable of yielding a filtrate which would give a very faint opalescence with both silver and hydrobromic acid; and this effect usually diminished upon long continued agitation. The method of determination used in this series was based upon this fact. Somewhat less silver than the amount required was added to the strontic bromide, and a very weak standard solution of argentic nitrate (the cubic centimetre contained a milligramme of silver) was dropped in until equivalent solutions of silver and hydrobromic acid produced equal opalescence in two similar pipetted portions of the supernatant liquid. Since the opalescence was so faint that one could only with difficulty see it at all under ordinary conditions, a piece of apparatus which may be named a "nephelometer" (νεφέλη, a cloud), was devised for detecting it. Two test-tubes, holding each just 30 c.c., were arranged in a wooden frame so that 2 centims. of the top of the tubes were in darkness. The bottoms of the tubes were fitted into the top of larger opaque tubes containing water, and were provided with closely fitting cylindrical shades, which could be raised or lowered independently over a graduated scale. All these contrivances prevented disturbing side reflections from the meniscus at the top of the tube and the rounded glass at the bottom. The two test-tubes were slightly inclined towards one another, so that the eye at a distance of 8 inches could look directly into both without change of position. Filled with pure water the tubes appear absolutely black, even when exposed to a strong light; but an absurdly small amount of precipitate, which no ordinary means could discover at all, makes a very evident cloudiness. By sliding the shades up and down a point may be found where the two tubes, containing solutions of different cloudiness, appear equal in depth of tone. The reason of this is that only the portion of the opalescence is visible upon which light is allowed to fall. Of course the intensities of the opalescence, and hence the quantities of precipitate, are then inversely as the length of the lighted portions of the two tubes.

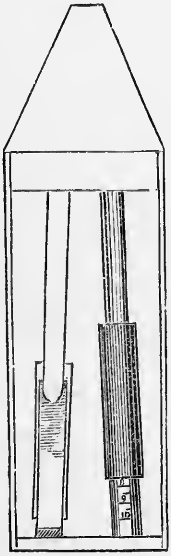


FIG. 3.

If care is taken to direct the light horizontally upon the tubes, considerable accuracy may be obtained with the apparatus, especially if the columns are nearly equal in cloudiness.

A pointed blackened roof with a small hole in the top for the eye is useful in excluding light from the surface of the liquid, thus rendering the comparison easier. The chief advantages in the apparatus lie in the facts that the two disks of light to be compared remain equal in size throughout the comparison, and that the eye is not confused by bright surface reflections. Two typical test series are given below. In each case one shade was adjusted at 10 centims. and the other was run backward and forward until apparent similarity was obtained.

(*a*). One tube contained 0·010 m.grm. of silver, and the other 0·0125 m.grm., measured by means of a very dilute standard solution. Both amounts were made up to 25 c.c., and 1 c.c. of hundredth normal hydrochloric acid was added to each. The opalescence in each was then compared after a thorough stirring and a short delay.

Heights of Columns appearing Alike.

	Stronger Solution. C.m.	Weaker Solution. C.m.
	8·7	10·0
	7·9	10·0
	6·9	10·0
	7·6	10·0
	8·4	10·0
	8·6	10·0
	8·9	10·0
Found ..	8·1	10·0
True value	8·0	10·0

(*b*). In a similar experiment one tube contained 0·025 m.grm. of silver, the other 0·0225 m.grm.

Heights of Columns appearing Alike.

	Stronger Solution. C.m.	Weaker Solution. C.m.
	8·8	10·0
	8·9	10·0
	8·2	10·0
	9·5	10·0
	8·9	10·0
	8·7	10·0
	8·9	10·0
	9·4	10·0
Found ..	8·9	10·0
True value	9·0	10·0

Some series were more accurate, others less so, than these, which serve to give a fair idea of the probable error of the method.

The details of the analysis must be evident from what has been said. The method is similar to Stas's third method for the determination of chlorine (*Proc. Amer. Acad.*, xxix., 86), except that of course the opalescence is very much fainter.

Below are given the tables containing the data and results of the three series; these will be comprehensible without further remark.

Ratio of Strontic Bromide to Silver.

First Series. Volhard's Method.

No. of Anal.	No. of Sp.	Weight of Strontic Bromide taken.	Total Weight of Silver taken.	Excess of Silver.	Weight of Silver corres. to Strontic Bromide.	Ratio $\frac{SrBr_2}{Ag_2}$.	Atomic Weight Sr.
		Grms.		M.g.			
1.	III.	1·49962	1·30893	1·38	1·30755	114·689	87·658
2.	III.	2·41225	2·10494	1·43	2·10351	114·677	87·633
3.	III.	2·56153	2·23529	1·72	2·23357	114·683	87·645
4.	V.	6·15663	5·3686	0·2	5·3684	114·683	87·644
		12·63003			11·01303	114·683	87·644

Ratio of Strontic Bromide to Silver.

Second Series. Abrahall's Method.

No. of Anal.	No. of Spec.	Weight of Strontic Bromide taken.	Weight of Silver required.	Ratio $\frac{SrBr_2}{Ag_2}$	At. wt. of Strontium.
		Grms.	Grms.		
5.	III.	1·49962	1·30762	114·683	87·645
6.	III.	2·41225	2·10322	114·693	87·667
7.	III.	5·24727	4·57502	114·694	87·668
8.	V.	6·15663	5·3680	114·691	87·663
		15·31577	13·35386	114·692	.87·663
Third Series. New Method.					
9.	IV.	2·9172	2·5434	114·697	87·675
10.	VI.	3·8946	3·3957	114·692	87·665
11.	VI.	4·5426	3·9607	114·692	87·664
12.	III.	5·2473	4·5750	114·695	87·671
		16·6017	14·4748	114·694	87·668

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1895.

Mr. A. G. Vernon Harcourt, President, in the Chair.

(Concluded from p. 48).

92. "*On some Physical Properties of the Chlorides of Gold.*" By T. K. Rose, D.Sc., A.R.S.M.

The melting-point of trichloride of gold is found to be 288° C., under a pressure of about two atmospheres of chlorine. Its density is 4·3, and that of the monochloride, 7·4. These determinations tend to show that the atomic volume of chlorine when in combination with gold is 4×5·1, instead of 3×5·1, the volume assigned to it by Schröder in the case of some of its other compounds. Mr. W. J. Pope found that volatilised crystals of trichloride of gold are crystalline aggregates, but that they cannot be referred to any system as they do not transmit the light from a sodium flame.

93. "*The Dissociation of Liquid Nitrogen Peroxide. Part II. The Influence of the Solvent.*" By J. Tudor Cundall.

The author measures colorimetrically the dissociation at different temperatures of solutions of nitrogen peroxide in fourteen "indifferent" solvents, viz.:—Chloroform, ethylene chloride, ethylidene chloride, methylene chloride, carbon tetrachloride, benzene, monochlorobenzene, monobromobenzene, ethyl bromide, ethylene bromide, bromoform, silicon tetrachloride, carbon disulphide, and acetic acid. He finds that the dissociation takes place in the same way, though to a different extent, in the various solvents; the extent of dissociation at any temperature being in the main an additive property, though probably modified by constitution. Thus the carbon atoms in a compound have very little influence on the dissociation power; those of hydrogen have more; then those of bromine and chlorine, whilst those of sulphur and silicon have most. Ethylene chloride is not so effective as ethylidene chloride.

The author compares his results with those of Mentschutkin (*Zeit. Phys. Chem.*, i., 611, and vi., 41), and brings evidence to show that, if the heat of dissociation of liquid nitrogen peroxide is the same as that calculated by van 't Hoff for the gas, any reaction that may take place between the dissolved substance and "indifferent" solvent is probably not exothermic.

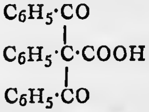
94. "*Condensation of Benzil with Ethylic Acetoacetate.*" By Francis R. Japp, F.R.S., and G. Druce Lander, B.Sc.

By heating a mixture of benzil and ethylic acetoacetate with sodium ethoxide in alcoholic solution, the two first-mentioned compounds condense according to the equation $2C_{14}H_{10}O_2+C_6H_{10}O_3=C_{34}H_{28}O_6+H_2O$. This condensation product is obtained as a sodium compound containing alcohol of crystallisation: $C_{34}H_{27}NaO_6,C_2H_6O$. Acetic acid liberates from this compound *ethylic anhydrodibenzilacetoacetate*, $C_{34}H_{28}O_6$, which crystallises from alcohol or from a mixture of ethylic acetate and light petroleum in flat needles or prisms, with bevelled edges, melting with decomposition at 210—211°. Although this compound contains the carbethoxyl group, it was not found possible to hydrolyse it to the corresponding acid, owing to the ease with which it is decomposed with regeneration of benzil.

By boiling this compound with alcohol containing a little sulphuric acid *cthylic ethylanhydrodibenzilacetoacetate*, $C_{34}H_{27}(C_2H_5)O_6$, was obtained, which was deposited from alcohol in slender prisms melting at 197°. It was readily hydrolysed by caustic potash. *Ethylanhydrodibenzylacetoacetic acid*, $C_{32}H_{23}(C_2H_5)O_6$, is deposited from benzene in microscopic matted needles melting at 216°. It is isomeric with the condensation compound.

Substituting isobutylic for ethylic alcohol in the foregoing etherification, *ethylic isobutylanhydrodibenzilacetoacetate*, $C_{34}H_{27}(C_4H_9)O_6$, was obtained. It crystallised from a mixture of benzene and light petroleum in minute needles, melting at 202°. On hydrolysis it yielded *isobutylanhydrodibenzilacetoacetic acid*, $C_{32}H_{23}(C_4H_9)O_6$, which was deposited from a benzene solution in slender needles melting at 237°.

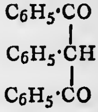
When the condensation compound was oxidised with chromium trioxide in acetic acid solution it yielded a monobasic acid, $C_{22}H_{16}O_4$, which crystallised from a mixture of ethylic acetate and light petroleum in needles melting at 200° with evolution of carbon dioxide. In this process of decomposition by heat the acid is converted into a compound $C_{21}H_{16}O_2$, which is deposited from alcohol in needles melting at 119—120°. The constitution of these two compounds may possibly be expressed by the formulæ—



$$\begin{array}{c} C_6H_5\cdot CO \\ | \\ C_6H_5\cdot C\cdot COOH \\ | \\ C_6H_5\cdot CO \end{array}$$

Phenyldibenzoylacetic acid.

and



$$\begin{array}{c} C_6H_5\cdot CO \\ | \\ C_6H_5\cdot CH \\ | \\ C_6H_5\cdot CO \end{array}$$

Phenyldibenzoylmethane.

Fuming hydriodic acid at its boiling-point converts the condensation product into a compound $C_{31}H_{24}O$, which crystallises from a mixture of ethylic acetate and light petroleum in short prisms melting at 187—188°:—

$$C_{34}H_{28}O_6+3H_2=C_{31}H_{24}O+C_2H_6O+CO_2+2H_2O.$$

Suspecting that the condensation product was a carbethoxyl derivative of anhydracetonedibenzil (Japp and Miller, *Trans.*, 1885, xlvii., 34), the authors reduced the latter compound with boiling hydriodic acid, and obtained the foregoing reduction compound $C_{31}H_{24}O$ (m. p. 187—188°) together with an isomeride crystallising from a mixture of ethylic acetate and light petroleum in pyramids melting at 155—159°.

The results do not permit of a conclusion being drawn as to the constitution of the condensation product. The constitution of anhydracetonedibenzil is also unknown.

95. "*On a Method for Preparing the Formyl Derivatives of the Aromatic Amines.*" By H. R. Hirst and J. B. Cohen, Ph.D.

Formamide reacts with the aromatic primary amines in presence of cold glacial acetic acid, forming formyl derivatives. The mixture is allowed to stand for a few hours, and the product poured into water. The resulting derivative is nearly pure, and the yield is very satisfactory. The reaction takes place according to the equation—

$$R'NH+HCONH_2+CH_3{\cdot}CO_2H = \\ =R'NH{\cdot}COH+CH_3{\cdot}CO_2NH_4.$$

The secondary aromatic amines containing an alkyl radicle only react on heating, whereas the tertiary amines and diphenylamine do not react even after continued boiling.

The formyl derivatives of the following bases have been prepared:—Aniline, ortho- and para-toluidine, α- and β-naphthylamine, phenyl- and orthotolyl-hydrazin, methyl- and ethyl-aniline, paraphenylenediamine, and benzidine.

96. "*A Modification of Zincke's Reaction.*" By H. R. Hirst and J. B. Cohen, Ph.D.

A small piece of aluminium foil coated with mercury, which is prepared by dipping the foil into a solution of mercuric chloride, is capable of bringing about a reaction between benzyl chloride, chloroform, &c., on the one hand, and aromatic hydrocarbons on the other. This reaction closely resembles that of Zincke, but takes place at the ordinary temperature. With benzyl chloride and benzene a satisfactory yield of pure diphenylmethane may be obtained. In a similar manner phenyltolylmethane and phenylxylylmethane have been prepared.

97. "*A Method for Preparing Cyanuric Acid.*" By W. H. Archdeacon, B.Sc., and J. B. Cohen, Ph D.

When urea in fine powder is heated in a sealed tube with the calculated quantity of phosgene in 20 per cent toluene solution, little action occurs until the temperature rises above 180°. A tube which had been heated for four hours at 170—180° showed very little pressure on opening; but after being re-sealed and heated for seven hours at 190° and eight and a half hours at 230°, great pressure was observed on opening the tube, and hydrochloric acid fumes were copiously evolved. The brownish microcrystalline product was separated by filtration and dried *in vacuo*. It amounted in two experiments to 133 and 127 per cent of the urea used. It dissolved without change in cold concentrated sulphuric acid, being re-precipitated in a crystalline form by water. It dissolved also in alkalis, and from the neutral solution in ammonia silver nitrate threw down a white amorphous precipitate.

The characteristic needles of the sodium salt, and the amethyst-coloured precipitate with copper ammonium sulphate solution, served to identify the compound as cyanuric acid.

The crude product gave the following result on analysis:—

I. 0·095 grm. gave 28·2 c.c. nitrogen at 17° and 737 m.m.
II. 0·1753 grm. gave 0·040 grm. H_2O and 0·179 grm. of CO_2.

	Theory for $(CONH)_3$.	Found.
C	27·91	27·85
H	2·33	2·53
N	32·56	33·38

The reaction probably occurs according to the equation $3CO(NH_2)_2+3COCl_2=2(CONH)_3+6HCl$.

98. "*The Oximes of Benzaldehyd and their Derivatives.*" By C. M. Luxmoore, B.Sc.

The paper contains an account of experiments undertaken with a view to throwing further light on the isomerism of the aromatic aldoximes. As already mentioned in a preliminary note by Professor Dunstan and the author (*Proc. Chem. Soc.*, 1893, 253), in examining the mechanism of the change of benzantialdoxime into benzsynaldoxime by hydrogen chloride, the previously unknown benzantialdoxime hydrochloride has been isolated; on solution it is converted into the syn-hydrochloride. The two isomeric sulphates have also been prepared. Since the change of the antioxime into its isomeride is always preceded by the formation of a derivative of the former, which then passes into the more stable syn-derivative, a stereo-chemical explanation of the isomerism is rendered probable.

By the action of methyl bromide on benzantialdoxime the hydrobromide of its "nitrogen" methyl ether is produced (m. p. 67°). This ether yields the same products of hydrolysis and reduction as the "nitrogen" methyl ether obtained from benzsynaldoxime. It differs from the latter in its lower melting-point and in the extreme readiness with which it is hydrolysed. The hydrobromide is stable, but the ether itself rapidly passes on standing into the isomeric syn-nitrogen ether. Structural formulæ are insufficient to explain the existence of the four isomeric ethers (two "oxygen" and two "nitrogen") which are known. Probably, therefore, the aldoximes themselves are stereo-isomeric; but both act tautomerically, and the synaldoxime reacts more readily in the sense of the isoximido formula than the antialdoxime does.

Treated with phosphorus pentachloride both oximes yield a little formanilide, but chiefly benzonitrile. Phosphorus trichloride converts benzantialdoxime into an extremely unstable chlorine derivative; with benzsynaldoxime it yields benzonitrile and hydrogen chloride instantaneously.

Almost all the stereo-chemical hypotheses equally well explain the isomerism of oximido-compounds of triad nitrogen; but in the case of derivatives with pentad nitrogen Pickering's theory is more in accordance with the facts than any other.

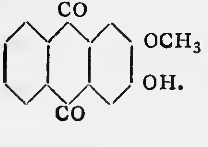
99. "*On a Colouring-matter from 'Lomatia ilicifolia' and 'Lomatia longifolia.'*" By Edward H. Rennie, M.A. (Sydney), D.Sc. (Lond.).

The author describes a yellow colouring-matter adhering to the seeds of two different species of *Lomatia*, a plant belonging to the order Proteaceæ. The colouring-matter is easily extracted by hot water, and is regarded by the author as *hydroxylapachol*. Its barium derivative closely resembles the barium derivative of hydroxyhydrolapachol described by Hooker. When treated with sulphuric acid under certain conditions, it is converted into *hydroxy-β-lapachone*. Other derivatives are described in the paper, and also an isomeric *hydroxylapachol*.

100. "*The Colouring and other Constituents contained in Chay Root.*" Part II. By A. G. Perkin and J. J. Hummel.

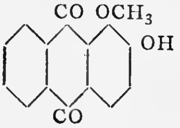
A previous examination of chay root (*Trans. Chem. Soc.*, 1893, 1160) showed that it contained rubichloric acid, two waxes, cane-sugar, ruberythric acid, alizarine, two dimethyl ethers of anthragallol (A) and (B), m. p. 209°, and 225—227°; an alizarine monomethyl ether, and *m*-hydroxyanthraquinone. By the investigation of very large quantities of the root, 2 cwts., obtained through the Imperial Institute, two new substances have been isolated.

One substance, $C_{15}H_{10}O_4$, was obtained as orange-coloured needles melting at 232°. When heated with hydrochloric acid to 180° it yielded hystazarin, and was found to contain one methoxyl group. It is therefore an *hystazarinmonomethyl ether*,—



A second constituent, $C_{16}H_{12}O_5$, formed minute orange-red needles melting at 212—213°, and its acetyl compound at 160°. It contained two methoxy groups, and by the action of hydrochloric acid at 180° was converted into anthragallol. It was consequently an anthragallol dimethyl ether, and it is interesting to note that chay root therefore contains the three dimethyl ethers of anthragallol.

Since the publication of the previous communication (*loc. cit.*), Schunck and Marchlewski (*Trans. Chem. Soc.*, 1894, 182) have prepared the alizarine β-monomethyl ether from alizarine. This is not identical with that found in chay root, which must consequently be the α-compound,



The readiness with which this is decomposed into alizarine by boiling with dilute alkalis, readily accounts for its non-production by the usual methods.

101. "*The Six Dichlorotoluenes and their Sulphonic Acids.*" By W. P. Wynne and A. Greeves, Assoc. R.C.S.

Sulphonic derivatives of the 1 : 2 : 5- and 1 : 3 : 4 dichlorotoluenes were described in a previous paper (*Trans. Chem. Soc.*, 1892, 1050, *et seq.*); the present communication deals with the remaining isomerides and their sulphonic acids.

1 : 2 : 3-*Dichlorotoluene* was prepared by three methods: (*a*) from 1 : 2 : 5-nitrorthotoluidine by chlorination, (*b*) from Lellman and Würthner's 1 : 2 : 3-nitracetorthotoluidide (m. p. 158°, *cf. Annalen*, ccxxviii., 239), and (*c*) from orthochlorotoluenesulphonic acid by nitration. It boils at 207—208° under 760 m.m. pressure, and on oxidation yields a dichlorobenzoic acid melting at 164° (*cf.* Seelig, *Annalen*, ccxxxvii., 162). On sulphonation two isomeric acids are obtained, which can be separated by means of their barium salts. The acid from the less soluble barium salt forms a very soluble *chloride*, crystallising in radiate needles, melting at 45°, and an *amide*, melting at 221°, whilst that from the more soluble barium salt is the 1 : 2 : 3 : 5-derivative, and like this yields a *chloride*, crystallising in well-defined prisms, melting at 85°, and an *amide*, melting at 183°.

1 : 2 : 4-*Dichlorotoluene* was prepared (*a*) from metatolylenediamine by Erdmann's method (*Ber.*, xxiv., 2769), (*b*) from 1 : 2 : 4-nitrorthotoluidine, and (*c*) from orthochlorotoluenesulphonic acid by nitration. It boils at 199—200° under 760 m.m. pressure. On sulphonation, it yields the 1 : 2 : 4 : 5-acid, characterised by the *chloride* crystallising in elongated scales, melting at 71°, and the *amide*, melting at 177°.

1 : 2 : 6-*Dichlorotoluene* was prepared from the 1 : 2 : 6-nitrorthotoluidine of Green and Lawson (*Trans. Chem. Soc.*, 1891, 1013). It boils at 199—200° under 760 m.m. pressure, and on oxidation yields a dichlorobenzoic acid melting at 139° (*cf.* Claus and Stavenhagen, *Annalen*, cclxix., 228). On sulphonation, an acid is obtained which gives a *chloride*, crystallising in prismatic needles, melting at 60°, and an *amide*, melting at 204°.

1 : 3 : 5-*Dichlorotoluene* was prepared from the 1 : 3 : 4 : 5-dichloroparatoluidine by Lellmann and Klotz's method (*Annalen*, ccxxxi., 321) and from the 1 : 2 : 3 : 5 dichlororthotoluidine of Claus and Stapelberg (*Annalen*, cclxxiv., 292). It boils at 201—202° under 760 m.m. pressure. On sulphonation, an acid is obtained which forms a very soluble *chloride*, melting at 45°, and an *amide*, melting at 168°.

To aid in the determination of the constitution of the dichlorotoluenesulphonic acids, the nitro-derivatives of the five known chlorotoluenesulphonic acids have been prepared and examined. For example, 1 : 2 : 4-orthochlorotoluenesulphonic acid on nitration gives as chief product the 1 : 2 : 4 : 5-nitro-acid, since the dichlorotoluenesulphonic acid obtained from it is identical with that obtained from 1 : 2 : 5-dichlorotoluene (*Trans. Chem. Soc.*, 1892, 1052). In like manner, 1 : 2 : 5-orthochlorotoluenesulphonic acid is shown to give as chief product the 1 : 2 : 4 : 5-nitro-acid, and as subsidiary product the 1 : 2 : 3 : 5 nitro-acid.

1 : 2 : 3-Nitrorthotoluidine is converted by Sandmeyer's method into the *nitrorthochlorotoluene*, which boils at 263° under 760 m.m. pressure, On reduction, this yields the 1 : 2 : 3-*orthochlorometatoluidine*, which boils at 228—229° under 760 m.m. pressure, and forms an *acetyl* derivative melting at 132°.

1 : 2 : 4-Nitrorthotoluidine in like manner yields the *nitrorthochlorotoluene*, which crystallises in pale yellow needles, melting at 65°, and the *orthochloroparatoluidine*, which boils at 245° under 760 m.m. pressure, and forms an *acetyl* derivative melting at 86°.

1 : 2 : 5-Nitrorthotoluidine on chlorination in the presence of iodine yields a *chloronitrorthotoluidine* melting at 168°. This is the 1 : 2 : 3 : 5-derivative, since, by eliminating the NH_2-radicle, it forms the 1 : 3 : 5-nitrochlorotoluene melting at 61°, the 1 : 3 : 5-chlorometatoluidine, characterised by its acetyl derivative melting at 151° (*cf.* Honig, *Ber.*, xx., 2419), and 1 : 3 : 5-dichlorobenzoic acid melting at 182°. By Sandmeyer's method the corresponding *nitrodichlorotoluene*, which crystallises in pale yellow needles melting at 83°, was obtained, and from this, by reduction, the *dichlorometatoluidine*, which crystallises in needles, melts at 88°, boils at 292° under 760 m.m. pressure, and forms an *acetyl* derivative melting at 187°.

1 : 2 : 6-Nitrorthotoluidine yields a *chlororthotoluidine*, which boils at 245° under 760 m.m. pressure, and forms an *acetyl* derivative melting at 154°.

The mixture of dichlorotoluenes obtained by chlorinating orthochlorotoluene under Seelig's conditions (*loc. cit.*) is being examined with the object of determining its constituents.

102. "*The Disulphonic Acids of Toluene and of Ortho- and Parachloro-toluene.*" By W. P. Wynne and J. Bruce. Assoc. R.C.S.

As is known (*cf. Trans. Chem. Soc.*, 1892, 1082), parachlorotoluene, on sulphonation, forms a product containing both the 1 : 2 : 4- and 1 : 3 : 4-sulphonic acids. Experiments have been undertaken with the object of estimating the relative proportions of these acids, both directly and by an examination of the disulphonic acids obtained by sulphonating parachlorotoluene with 20 per cent anhydrosulphuric acid. For the purposes of comparison, chloroacids have been prepared by Sandmeyer's method from the paratoluidinemono- and di-sulphonic acids of known constitution.

The paratoluidinedisulphonic acids obtained by Richter from the 1 : 3 : 4- and the 1 : 2 : 4-paratoluidinemonosulphonic acids (*Annalen*, ccxxx, 314, 331) are shown to be the 1 : 3 : 4 : 6- and 1 : 2 : 4 : 6-derivatives respectively. The former, by elimination of the NH_2-radicle, gives a toluenedisulphonic acid identical with that obtained from the 1 : 2 : 5-orthotoluidinesulphonic acid by the xanthate method.

1 : 2 : 4 - Parachlorotoluenesulphonic acid, prepared from the corresponding amido-acid, gives a sparingly soluble *barium* salt, a *chloride* melting at 23—24°, and an *amide* melting at 142°. On sulphonation with 20 per cent. anhydrosulphuric acid, it yields, as sole product, an acid identical with that obtained from the 1 : 2 : 4 : 6-paratoluidinedisulphonic acid.

1 : 3 : 4 - Parachlorotoluenesulphonic acid, obtained from the corresponding amido-acid, gives an easily soluble *barium* salt, a *chloride* crystallising in plates melting at 54°, and an *amide* melting at 154°. On sulphonation with 20 per cent anhydrosulphuric acid, two disulphonic acids are obtained, the chief product being the 1 : 3 : 4 : 6-derivative, since it is identical with the acid obtained from the 1 : 3 : 4 : 6-paratoluidinedisulphonic acid.

Parachlorotoluene, on sulphonation with 20 per cent anhydrosulphuric acid under similar conditions, gives a mixture of the 1 : 2 : 4 : 6- and 1 : 3 : 4 : 6-disulphonic acids in the proportions of about three parts of the former to one of the latter.

The 1 : 2 : 3 : 5-orthotoluidinedisulphonic acid prepared by Hasse's method (*Annalen*, ccxxx., 286), and shown to be identical with Hasse's product by conversion into the bromotoluenedisulphonic chloride, gives, by the hydrazine method of eliminating the NH_2-radicle, a toluenedisulphonic acid, which differs from that described by Hasse, since its chloride (Cl found 24·5, Hasse 25·9, theory 24·6) melts, not at 132°, but at 95°.

1 : 2 : 5-Orthochlorotoluenesulphonic acid gives, on further sulphonation, a product which seems to differ from that obtainable from Hasse's acid by Sandmeyer's method, and is being further examined.

In addition to the known 1 : 2 : 4-, 1 : 2 : 5-, and 1 : 3 : 5-toluenedisulphonic acids, the following have been prepared :—

1 : 2 : 6-*Toluenedisulphonic acid*, obtained from the 1 : 2 : 4 : 6-paratoluidinesulphonic acid, by eliminating the NH_2-radicle, forms a *potassium* salt crystallising with $1\frac{1}{2}H_2O$ in minute prisms, and a *chloride*, crystallising in scales, melting at 99°.

1 : 3 : 4-*Toluenedisulphonic acid*, obtained from the 1 : 3 : 4-paratoluidinemetasulphonic acid by the xanthate method, forms a mono-hydrated *potassium* salt crystallising in needles, and, on treatment with phosphorus pentachloride, yields the *chloride*, which crystallises from benzene with $\frac{1}{2}$ mol. proportion of benzene in large prisms melting at about 60°, and from petroleum spirit in scales melting at 111°.

103. "*Contributions to our Knowledge of the Aconite Alkaloids.*" Part XII. "*The Constitution of Pseudaconitine. Preliminary Notice.*" By Wyndham R. Dunstan, F.R.S., and Francis H. Carr.

Pseudaconitine is the name given by Alder Wright to the highly toxic alkaloid contained in Nepaul aconite (*Aconitum ferox*). It is a crystalline base, melting at 104—105°, whose composition is expressed by the formula $C_{36}H_{49}NO_{12}$. When hydrolysed it furnishes, according to Alder Wright and Luff (*Trans. Chem. Soc.*, 1878), *pseudaconine* and one molecular proportion of *dimethylprotocatechuic acid* (veratric acid),—

$$C_{36}H_{49}NO_{12}+H_2O=C_{27}H_{41}NO_9+C_9H_{10}O_4.$$

The authors are engaged in a re-investigation of this alkaloid in the light of their recent work on the constitution of aconitine derived from *Aconitum napellus* (*Trans. Chem. Soc.*, 1894, 176, 290).

The pseudaconitine employed by the authors was extracted from the roots of *Aconitum ferox*, some of which were provided by the Government of India through the Imperial Institute. The highly-purified crystalline base melted at 201°, that is, nearly 100° higher than the point recorded by Wright and Luff; this melting-point was not changed by fractional crystallisation.

When heated slightly above its melting-point, pseudaconitine loses a molecular proportion of acetic acid, leaving a new base, which it is proposed to name *pyropseudaconitine*. This alkaloid, on hydrolysis, loses a molecular proportion of dimethylprotocatechuic acid, furnishing *pyropseudaconine*.

On complete hydrolysis with alkali, pseudaconitine yields, in addition to the dimethylprotocatechuic acid observed by Wright and Luff, a molecular proportion of acetic acid, which was identified and estimated in the manner described in the authors' previous paper on aconitine.

When pseudaconitine sulphate is heated in a closed tube with water, it suffers, like aconitine, partial hydrolysis, the acetyl group alone being eliminated, producing a molecular proportion of acetic acid. In this action a new alkaloid is formed, corresponding with the benzaconine derived in a similar manner from aconitine, which the authors propose to name *veratrylpseudaconine*. This substance is a crystalline base (m.p. 181°) which, when hydrolysed, furnishes pseudaconine and dimethylprotocatechuic acid (veratric acid).

There is therefore a close resemblance between the constitution of aconitine and of pseudaconitine, both alkaloids undergoing hydrolysis in a similar manner. The molecule of each alkaloid contains an acetyl group; but in pseudaconitine the benzoyl group of aconitine is replaced by the veratryl group, aconitine being *acetylbenzaconine*, and pseudaconitine *acetylveratrylpseudaconine*. As far as the authors' investigation has proceeded, pseudaconine appears to be distinctly different from the aconine derived from aconitine. There is little reason at present to doubt that the crystalline highly active alkaloid isolated by the authors is identical with Wright's pseudaconitine, but further evidence on this point is being obtained.

Library.

The Library will be closed during the last fortnight in August for cleaning and the annual revision of the Catalogue. Fellows are requested to return all books in their possession not later than August 15th.

Research Fund.

The following grants have been made by the Council on the recommendation of the Research Fund Committee :—

£30 to Messrs. J. J Hummel and A. G. Perkin, for the investigation of certain natural colouring-matters.

£10 to Dr. H. Ingle, for the purchase of various aldehydes, ketones, and hydrazine, to continue his work on stereoisomeric osazones.

£10 to Dr. J. J. Sudborough, to continue his work on diortho-substituted benzoic acids.

£15 to Mr. E. Haworth, for the synthesis of an acid having the composition $C_8H_{14}(COOH)_2$, and the comparison of its properties with those of camphoric acid.

£5 to Mr. R. E. Doran, for a research on the preparation of mustard oils by the reaction of chlorocarbonic esters with lead thiocyanate.

£15 to Dr. W. A. Bone, to continue a research on the substituted succinic acids, and on the behaviour of various trimethylene compounds on treatment with the sodium compound of ethylic malonate.

£10 to Dr. B. Lean, to extend his work on the derivatives of ethylic butane tetracarboxylate.

£20 to Dr. J. Walker, for an investigation of the conditions of equilibrium between the cyanates and the corresponding ureas.

NOTICES OF BOOKS.

The Mechanical Auxiliaries of Chemical Technics. ("Die Maschinellen Hilfsmittel der Chemischen Technik"). By A. Parnicke, Civil Engineer, formerly Head-Engineer at the Grielheim Chemical Works. With 337 Illustrations. Frankfurt-on-Mayn: H. Bechold. 1894. 8vo., pp. 320.

That a work of this character should have been found requisite is a striking proof of the development of the chemical industries in Germany. It is now found necessary that the technical chemist should possess a clear and comprehensive acquaintance with the mechanical auxiliaries which he has to employ. On the small scale in the laboratory, the skilled hand of the chemist brings into mutual contact in their due proportions and conditions the substances which have to react. But when we transfer the process from the laboratory to the works, and employ hundred-weights in place of grms., there arises a new task.

Mechanical auxiliaries have to be devised which may take the place of the skilled hand, and on their presence or absence, or rather on their perfection or defectiveness, the whole question of success or failure may turn.

To take an instance. The ammonia-soda process was invented and patented in Britain long before the days of Solvay. But the mechanical appliances for carrying out the reaction were so imperfect that the process was a commercial failure until better appliances were devised by Solvay and his coadjutors, when ammonia-soda became a formidable rival to the Leblanc process. Other similar cases might readily be found, and it will strike the reader that reactions have been conceived which remain a dead-letter because the arrangement and construction of the proper plant has presented difficulties not yet surmounted.

Hence the technical chemist, without seeking to become a jack-of-all-trades, ought to have a general acquaintance with the appliances used for the various types of chemical processes, so that he may select such as are likely to suit his exact purpose. He must be able to come to an understanding with the mechanical engineer, and to explain precisely what he wants. Hence the work before us, compiled as it is by an experienced specialist, will be of great service to graduates of universities and polytechnics on their entrance into a practical career.

After a few useful generalities, the author treats systematically of sources of power, of the transmission of power, and of contrivances for the conveyance of material products. Under this last heading is included the removal of offensive or pernicious vapours. These, it is said, are not to be conveyed into the soil, though the author, very questionably, seems to sanction their direct introduction into water.

The fourth section discusses machines for comminution, including disintegrators, indigo-mills, and colour-mills. Mixing machines are described adapted for solids alone, liquids alone, and for incorporating solids with liquids and gases.

Next follow appliances for fusion, solution, and lixiviation, for concentration and vaporisation, for mechanical separations (including extraction and fractionation). Here are included filter-presses, appliances for separation by crystallising, by sublimation, and by refrigerating machines.

Mention is made of the increasing preference shown for the ammonia process as compared with the use of carbonic acid.

Desiccatory apparatus forms the subject of the ninth chapter, and in the tenth we have an account of apparatus for determining weight, temperature, pressure, and draught of gaseous current. An instrument devised by Arndt bears the remarkable name of the "econometer," and is here figured. It consists of a gas balance depending on a novel principle, and fixed in an air-tight case. The illustrations of the work are not only numerous, but for the most part very well drawn. Many of them, however, have a very annoying fault; the lettering is done, not with printing characters, but with script, and to make matters worse, with German script. As instances we may mention Figs. 202, 203, 224, &c. This is the more remarkable as the larger portion of the illustrations are lettered in a rational manner with printing characters.

How Shall Young Men be Educated in Applied Chemistry? By P. T. Austen, Ph.D., F.C.S., Professor of Chemistry in the Brooklyn Polytechnic Institute.

Concerning this essay we may say that, in part, Prof. Austen's advice to students is exceedingly judicious, and his demands thoroughly rational. But in part it must be confessed that his requirements are exorbitant, leading merely to a waste of time and of brain-power. What must be thought, *e.g.*, of the following programme? "A thorough grounding in history, the elements of law, political economy, metaphysics, logic, ethics, and literature should be effected." We submit that to the man of science history, other than the history of discovery and invention and their treatment by the world, is little better than fossil gossip; political economy and metaphysics must rank as a waste of time. The same should be remarked concerning mere ratiocinative logic, ethics, and literature. The elements of law are admissible merely as far as patents and sanitary regulations are concerned. On other matters, and on general principles, in as far as such can be said to exist, the technical chemist may well be referred to solicitors and counsel, remembering that his opinion on legal questions will only be received by the courts with derision.

The technical chemist will, of course, require to be well grounded in physics, especially in thermotics, optics, and electricity. Nor should mathematics be overlooked; but, on the principle of the division of labour, the "business side of industrial chemistry" had better be left to book-keepers and accountants.

A knowledge of the German and French languages is, of course, indispensable.

Much more useful to the technical chemist than metaphysics, ethics, and literature, will be botany and zoology. He may often be called upon to study the applicability of newly-discovered animal or vegetable products and the ways of combatting new parasites.

The author gives also moral lessons. The young works' chemist is told to be "honest to a fault"—an expression difficult to understand. He certainly should not cook results, but for telling the whole truth and nothing but the truth he may earn scant gratitude. We could point out a chemist who in his young days got into dire disgrace for reporting the presence of a serious percentage of arsenic in a sulphur ore just taken into stock, and was cautioned in future to determine nothing in the ores but sulphur, copper, and silver. If we, in turn, may give a piece of advice, we would caution every young technical chemist to shun any industrial establishment where a "self-made man" is in course of formation.

An excellent recommendation given by Prof. Austen is that the more advanced students in technical chemistry should not merely seek to make new substances by well-known methods—as is largely done, especially in Germany—but should be practised in producing known substances by new methods.

The author's essay abounds in suggestions of the highest importance, but we are led to question whether in these days the chemical student, if trained on his lines, would not be overwhelmed with matter of very secondary value.

University of Wyoming, Laramie, Wyoming. Departments of Chemistry and Mechanical Engineering. Special Bulletin. January, 1895. *The Heating Power of Wyoming Coal and Oil;* with a Description of the Bomb Calorimeter. By Edwin E. Slosson, Professor of Chemistry, and L. C. Colburn, Professor of Mechanical Engineering.

The authors give a table of the heating-power of Wyoming coal, and its proximate analysis. They discuss the varied efficiency of bodies, mentioning that only from 45 to 85 per cent of the theoretical evaporation power is actually obtained.

The Wyoming mineral oils are said to possess nearly double the heating capacity of the coals from the same region. The oils are said to be much like the Baku oils.

The methods of determining heating-power are next considered. Concerning the boiler test it is admitted that approximately accurate results can be obtained only from an experimental plant. The disadvantages are that the experiment is always a test of the efficiency of the furnace and boiler, and of skill in firing, rather than a determination of the absolute value of the fuel.

Elementary chemical analysis is a tedious and delicate process, the rather as the carbon may exist in different states which have not identical heats of combustion.

The authors recognise calorimetry as the most satisfactory method of determining the heating-power of a fuel, For this purpose they prefer the apparatus of Mahler, a cheaper modification of the celebrated bombe calorimetrique of Berthélot. Mahler's instrument is described and figured, and the corrections necessary in its use are given.

Year-Book of Organic Chemistry. Edited by GAETANO MINNUNI, of Palermo. Vol. I., 1893. With a Preface by ERNST VON MEYER. Large 8vo., pp. xiv. and 882. Leipzig: J. A. Barth. 1895.

THE author endeavours to collect in a single volume all newly-observed facts in organic chemistry, the results both of experiments and speculation. The volume for 1893 has already appeared, and that for 1894 will, it is hoped, be issued in the course of the present year.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 1, July 1, 1895.

At the meeting of July 1st Herr Schwarz was elected a correspondent of the Section of Geometry, *vice* the late Neumann; Baron Müller was elected a correspondent of Botanical Section, *vice* the late Pringsheim; and Dr. Engelmann was elected a correspondent of the Section of Medicine and Surgery, *vice* Herr Heidenhain.

This issue contains a short obituary notice of Professor Huxley, a correspondent of the Section of Anatomy and Zoology.

Determination of Small Quantities of Arsenic.—Ad. Carnot.—This paper will be inserted in full.

Oxidation Products of Benzyliden-camphor and of Benzyl-camphor. Nitrosate and Nitronitrite of Benzyliden-camphor. — A. Haller. — If benzyliden-α-benzyl-camphor are submitted to the action of oxidising agents they are ruptured at the point of attachment of the aromatic radicle, and the two nuclei behave then in the oxidising medium as if they were free.

On Paratungstic Acid.—L. A. Hallopeau.—It is easy to obtain solutions of paratungstic acids presenting all the known reactions of the paratungstates, and becoming converted into metatungstic acid on ebullition, just as the paratungstates are transformed into metatungstates. Paratungstic acid therefore really exists as Laurent maintained, but the little stability of its molecule caused it to be split up into tungstic acid and water on the simple concentration of its solutions. This fact alone distinguishes it from Graham's colloidal tungstic acid, which may be evaporated to dryness and heated to 200° without decomposition.

Determination of Alumina in Phosphates.—Henri Lasne.—This paper will be inserted in full.

On Sodium Amidide.—M. de Forcrand.—A thermochemical paper, not adapted for useful abstraction.

Phosphoric Ethers of Allylic Alcohol. Allylphosphoric Acid. — J. Cavallier. — Allylphosphoric acid has the composition $PO_4C_3H_5H_2$. With coloured reagents it behaves like most of the oxy-acids of phosphorus. Neutrality with methyl orange is obtained by the addition of 1 mol. of soda and neutrality with phenolphthalein by 2 mols. It forms two series of salts: neutral salts, $PO_4C_3H_5M_2$, and acid salts, $PO_4C_3H_5MH$. The author describes the most important salts of both series.

Preparation and Conductivity of New Cyanomethinic Ethers.—J. Guinchant.—Not admitting of useful abstraction and not of sufficient moment to claim insertion in full.

No. 2, July 8, 1895.

Action of Zinc Chloride upon Resorcine.—E. Grimaux.—The author obtains a substance fusible at 225°. It forms small colourless needles soluble in alcohol, acetone, sparingly soluble in ether, and soluble in 100 parts of boiling water. Its cold watery solution has a blue fluorescence, which is stronger if dissolved in alkalis, in ammonia, or in concentrated sulphuric acid. This substance is identical with umbelliferone, $C_9H_6O_3$. Another substance formed, $C_{24}H_{18}O_5$, is fusible at 264°. It is insoluble in water, soluble in alcohol, acetone, and ether.

Volumes of Salts in their Aqueous Solutions.—Lecoq de Boisbaudran.—This paper requires the accompanying diagram.

On Diphenylanthrone.—A. Haller and A. Guyot.—The researches of the authors show that the compound $C_{26}H_{18}O$ obtained by various procedures enumerated may be considered as diphenylanthrone. As the constitution of this substance is established, we are warranted in attributing to phthalyl tetrachloride, fusible at 88°—a scheme which makes of it a disymmetric molecule. Phthalyl dichloride contains tetrachloride.

Direct Spectral Analysis of Minerals and of certain Melted Salts.—A. de Gramont.

Determinations of the Solubility of Some Organic Compounds in Carbon Disulphide at very Low Temperatures.—Henryk Arctowski.—This memoir cannot be inserted without the insertion of the complicated diagram of curves.

Certain Oxidising Properties of Ozonised Oxygen, and of Oxygen exposed to the Sun's Rays.—A. Besson.—The author has formerly shown that ozonised oxygen acts upon perchloric ethylene, C_2Cl_4, forming, as the main product, trichloracetyl chloride, CCl_3COCl, and as an accessory product carbonyl chloride, $COCl_2$. He has since found that the same products are equally formed if dry oxygen is caused to act upon C_2Cl_4 in presence of direct solar light. Ozonised oxygen and dry oxygen, in presence of sunlight, react energetically upon the phosphorus iodides, setting free iodine, and forming complex products containing phosphorus, oxygen, and iodine.

Action of Nitric Oxide upon certain Metallic Chlorides, *i.e.*, Ferrous Chloride and the Bismuth and Aluminium Chlorides. — V. Thomas. — The yellowish brown compound formed from the ferrous chloride corresponds in composition with the compound obtained by saturating a solution of ferrous chloride with nitric gas at temperatures between 12·5° and 25°. Bismuth chloride exposed to the action of nitric oxide takes a yellowish colour, but the reaction is complete only after the lapse of several days. The compound ultimately obtained has the composition $BiCl_3NO$. The corresponding aluminium compound has the composition Al_2Cl_6NO. It has a pale yellow colour. Both the above compounds are highly hygroscopic, and the aluminium compound fumes on exposure to the air.

Action of the Halogens upon Methylic Alcohol.—A. Brochet.—This paper is not adapted for abstraction.

On a Physical Theory of the Perception of Colours.—Georges Darzens.

Revue Universelle des Mines et de la Metallurgie. Vol. xxx., No. 2.

This issue contains no chemical matter.

MISCELLANEOUS.

Preliminary Researches on the Hydrolysis of the Aqueous Solutions of Mercuric Chloride. — Henryk Arctowski. — The author has the ultimate purpose of expounding our entire knowledge on the chemical action of water upon salts. For the present he restricts himself to the case of mercuric chloride.—*Zeitschrift fur Anorg. Chemie.*

Preservation of Wheat.—M. Balland.—The author, quoting Duhamel du Monceau, mentions an experiment made on 94 cubic feet of wheat of the crop of 1743, which he had preserved for more than six years with the sole precaution of occasional ventilation, and which was not in the least impaired. Parmentier mentions that in 1774 the King and the royal family tasted bread made of wheat which had been kept for 221 years, and which had been deposited in the citadel of Metz since 1523. The method of preservation is not mentioned.—*Comptes Rendus*, cxx., No. 25.

City and Guilds of London Institute. — The Diploma of "Associate of the City and Guilds of London Institute" has been conferred by the Council of the Institute upon the following matriculated students, who have this year successfully completed the full course of instruction at the Central Technical College:—

Civil and Mechanical Engineering.—H. S. Andrewes, F. G. Arnould, J. E. Chapman, H. E. Fenwick, C. S. Hainworth, E. W. Hainworth, B. H. M. Hewett, E. W. Hummel, F. T. W. Lewis, F. E. Morgan, R. E. Reeves, H. Robinson.

Applied Physics and Electrical Engineering. — J. M. Barr, S. Beeton, C. Brandeis, W. M. Carver, A. D. Constable, S. Gilford, F. S. Grogan, A. C. Hanson, G. S. Hewett, C. D. Le Maistre, P. G. Phelps, W. Reilly, W. Roberts, H. G. Solomon, R. J. J. Swann, C. P. Taylor, E. L. Thorp, E. L. Webb, N. J. Wilson.

Applied Chemistry. — W. G. Bennett, W. A. Davis, W. T. Gidden, C. Revis, E. M. Rich, P. Spencer.

THE CHEMICAL NEWS.

Vol. LXXII., No. 1863.

A SCHEME FOR QUALITATIVE ANALYSIS OF A SOLUTION CONTAINING HYDRIC SULPHIDE, HYDROSULPHIDE, SULPHIDE, POLYSULPHIDE, THIOSULPHATE, SULPHITE, AND SULPHATE.

By W. P. BLOXAM, B.Sc. (Lond.).

In the Chemical News (lxxii., p. 39) there appears a communication from R. G. Smith, B.Sc., entitled "The Detection of Sulphates, Sulphites, and Thiosulphates, in Presence of Each Other." In this communication the author provides for the detection of sulphates, sulphites, and thiosulphates, and in conclusion states that "Hydrosulphuric acid would interfere with these reactions, and ought to be eliminated by bubbling carbon dioxide through the solution until the gas escaping from the tube no longer darkens lead-paper."

Without offering further criticism than that the presence of hydric sulphide vitiates entirely any attempt to separate sulphate, sulphite, and thiosulphate, whilst the method recommended for its removal is tedious, an outline of process is here given which has proved satisfactory in dealing with solutions containing normal sulphides, polysulphides, hydrosulphide, free hydric sulphide, sulphite, sulphate, and thiosulphate.

The necessity for such a process arose in the course of an investigation of the products of decomposition, on air exposure, of the laboratory agent known either as ammonium sulphide or ammonium hydrosulphide. The results of this investigation were communicated to the Chemical Society on June 15th, 1893, the paper being entitled "The Sulphides and Polysulphides of Ammonium." An abstract of this paper appeared in the *Proceedings of the Chemical Society*, Oct. 19th, 1893. The paper appeared at length in the *Journal of the Chem. Soc. Trans.* (lxvii., April, 1895). In it the following statement occurs (p. 278):—"The first point was to determine what ammonium compounds, other than sulphide and polysulphide, were present, and this involved the removal of sulphide and polysulphide, and the recognition in the filtrate of sulphite, thiosulphate, and sulphate. A scheme for separation is given by Fresenius ('Chemical Analysis—Qualitative, translated by C. E. Groves from the 15th German Edition,' p. 194), but it was found to require modification before successful results could be obtained, owing to the difficulty of removing the last traces of hydrogen sulphide. An account of the modified method of analysis will appear in another journal."

The author had in view publication in the Chemical News, and the appearance of Mr. Smith's paper induces him to make good his neglect.

The statement of Fresenius is as follows:—"When, as is often the case, it is required to find sulphites and hyposulphites of the alkalies in presence of alkaline sulphides, solution of sulphate of zinc is first added until the sulphide is decomposed; the sulphide of zinc is then filtered off, and one part of the filtrate is tested for hyposulphurous acid by addition of acid, another portion for sulphurous acid with nitroprusside of sodium, &c."

The treatment prescribed by Fresenius (*Ibid.*, p. 193) for the detection of sulphurous acid is as follows:—"If an aqueous solution of an alkaline sulphite is carefully neutralised with acetic acid, or bicarbonate of soda is added to it, according as it has an alkaline or acid reaction (excess of the bicarbonate is without effect, but excess of caustic alkali or simple carbonate, or of carbonate of ammonia, prevents the reaction), and a relatively large amount of solution of sulphate of zinc, mixed with a very small quantity of nitroprusside of sodium, be then added, the solution will become red if the quantity of the sulphite present is not too small; when, however, the amount of sulphite is very minute, the colouration makes its appearance only after the addition of some solution of ferrocyanide of potassium. If the quantities are not altogether too minute, a purple-red precipitate will form on the addition of the ferrocyanide of potassium (Bödeker). Hyposulphites of the alkalies do not show this reaction."

Being unable to obtain by purchase ammonium sulphite or ammonium thiosulphate in a state of purity, Mr. W. B. Giles, F.I.C., kindly undertook their preparation, and was eminently successful Analysis of the pure salts showed the following composition:—

$$2(NH_4)_2SO_3+3H_2O \text{ and } (NH_4)_2S_2O_3.$$

Experiments were made with mixtures of these salts according to the method of Fresenius. It was found, however, that contrary to the statement of Fresenius (*loc. cit.*) the presence of excess of ammonia enhanced the delicacy of the test for sulphite. Experiments demonstrated the possibility of detecting very small traces of sulphite mixed with excess of thiosulphate

On enlarging the scope of experiments so as to detect sulphite and thiosulphate in a solution containing sulphide and polysulphide, difficulty was experienced in getting rid of the last traces of hydric sulphide by precipitation as zinc sulphite. The solution being treated as recommended with zinc sulphate, and the precipitate removed by filtration, any trace of hydric sulphide left in the filtrate effectually masks the red colouration given by sulphite, the ordinary reaction of sulphides with sodium nitroprusside taking its place; experiments showed that addition of solution of cadmium sulphate would determine the complete removal of hydric sulphide. It was consequently employed in place of zinc sulphate, but the sulphite reaction was not obtained on adding nitroprusside and ferrocyanide. On addition to the filtrate of zinc sulphate, however, the reaction for sulphite was obtained, showing that the presence of cadmium sulphate did not prevent the detection of sulphite, whilst it effected the complete removal of hydric sulphide. Solution of cadmium chloride was employed with similarly successful results, and solution of zinc chloride was successfully substituted for one of zinc sulphate, with a view of eliminating sulphur compounds from the reagents used. Using mixtures of sulphide, polysulphide, sulphite, and thiosulphate, the influence of the following substances on the test was investigated, viz., ammonium chloride, ammonium carbonate, and free ammonia, the results indicating that they did prevent the detection of sulphite. A modified method of testing was accordingly adopted. A mixture of solutions of zinc chloride, cadmium chloride, ammonium chloride, and ammonia, was made in a stoppered cylinder. To this was added the solution containing sulphide, polysulphide, sulphite, and thiosulphate of ammonium. From time to time the mixture was gently agitated, and the air of the cylinder tested with paper moistened with solution of ammoniacal plumbic acetate. When the air was proved free from hydric sulphide, filtration was effected, and a few drops of the clear filtrate tested with solution of ammoniacal silver nitrate. If no colouration or precipitation was observed, the tests for sulphite and thiosulphate were then made. It was found by this method that even very small traces of sulphite could be detected with certainty. Experimenting in this fashion upon laboratory samples of coloured ammonium sulphide, it was determined that they contained thiosulphate, but only traces of sulphite. Under these circumstances it was suspected that during the progress of the test oxidation had taken place, sulphite becoming sulphate. Accordingly the filtrates, after separation of sulphide and polysulphide, were rendered strongly acid with hydric chloride (free from chlorine), and boiled to expel sulphur dioxide. The deposited sulphur was filtered off, and the filtrate tested for sulphate. Only the slightest traces could be detected, and these were attributed to the imperfect washing of hydric sulphide during saturation of ammonia with gas generated by the action of hydric sulphate on ferrous sulphide.

It being established that oxidation of sulphite did not occur in the course of analysis, experiments were now made upon mixtures containing sulphide, hydrosulphide, polysulphide, sulphite, thiosulphate, and sulphate of ammonium.

The solution was treated as previously described, with the mixture of zinc chloride, cadmium chloride, ammonic chloride and ammonia, and the filtrate (containing sulphite, thiosulphate, and sulphate) divided into two portions. One portion was treated as previously described for the detection of sulphite and thiosulphate. The other portion was treated as follows, for the detection of sulphate in presence of sulphite and thiosulphate:—The solution, after addition of a small quantity of pure sodic hydric carbonate, was placed in a flask, the cork of which was pierced by three holes. Through an inlet tube a current of washed carbon dioxide was admitted, and an outlet tube was provided dipping below the surface of water. Through the third hole, a small stoppered separating funnel passed, the tube reaching nearly to the bottom of the flask.

Through the cold solution a current of washed carbon dioxide was passed, and the liquid gradually raised to the boil. When all air was expelled, hydric chloride (free from chlorine) was cautiously admitted by the stoppered separating funnel. When excess of acid had been added the solution was boiled down to one-fifth of its original bulk, the current of carbon dioxide being maintained. The concentrated liquid was filtered from deposited sulphur, and a portion of the filtrate tested with ammoniacal silver nitrate to guard against undecomposed thiosulphate. If found to be free the remainder was tested for sulphate.

By these methods mixtures containing sulphide, hydrosulphide, polysulphide, sulphite, sulphate, and thiosulphate, have been successfully treated.

Some experiments have been made with a view to detecting the constituents of mixtures containing polythionates in addition to the sulphur compounds already dealt with, and the results will be communicated to the Chemical News in due course.

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PREPARATION OF THIOACETIC ACID, AND ITS IMPORTANCE FOR CHEMICO-LEGAL INVESTIGATIONS.

By ROBERT SCHIFF.

Some months ago I proposed to abandon, in analytical operations, the unpleasant and tedious use of sulphuretted hydrogen, and to apply in its stead thioacetic acid.

This convenient procedure has hitherto been adopted in but few laboratories, chiefly, as I learn, from the difficulty of preparing large quantities of thioacetic acid by the known methods. The methods of preparation described in chemical literature are all useless. Even that of Kekulé and Linnemann with phosphorus pentasulphide and glacial acetic acid gives enormously bulky black tumid masses, which at once fill the largest vessels, and compel the distillation to be broken off. By the following procedure we may work with any quantity at pleasure.

One part by weight of powdered phosphorus pentasulphide is mixed with ½ part by weight of fragments of glass (not too small) and 1 part of glacial acetic acid, and the mass is placed in a glass vessel fitted with a thermometer and an ascending condenser, and heated upon the wire gauze with a luminous flame. The reaction begins without any troublesome tumefaction, and is easily regulated by means of the flame.

When the temperature of the vapours has risen to about 103°, the process is interrupted. The yellow product is rectified, and the portion which passes over between 92° and 97°—pure thioacetic acid—is used, either in the free state as a 6 per cent aqueous solution, or as a salt in a 30 per cent feebly ammoniacal solution. We thus obtain pure thioacetic acid amounting almost to one-third of the acetic acid used. For each operation I use in a 2 litre flask 300 grms. phosphorus pentasulphide, 150 grms. broken glass, 300 grms. glacial acetic acid, and obtain 97 to 100 grms. of rectified thioacetic acid. This quantity, which does not require an hour to prepare, forms 300 c.c. of thioacetic solution, and suffices for more than 150 ordinary qualitative operations.

In the glass vessels there is left a hard black mass, which can be removed by heating with soda-lye. To save the trouble of cleansing, I use the well-known wine flasks common in Tuscany. These, without their straw cases, cost about 7 centimes; they are made of good thin green glass, and contain 2¼ to 2½ litres. I cut off two-thirds of the neck, melt off the aperture, inserting it in an ascending T-tube. When the reaction is completed the flask is thrown away.

All the operation is performed under a good draught-hood with a large flame burning in order to burn all escaping gases of an evil odour.

This thioacetic method is, as it appears to me, important for the qualitative and quantitative recognition of arsenic in chemico-legal investigations. I have formerly mentioned that if a hydrochloric solution of arsenious or arsenic acid is boiled with thioacetate for about a minute, when the liquid is cold the arsenic is found to have been quantitatively precipitated from the clear liquid.

The difficulty of maintaining a long-continued current of hydrogen sulphide, absolutely free from arsenic—as required for judicial purposes—is well known. On the contrary, rectified thioacetic acid is always absolutely free from arsenic.—*Berichte*, xxviii., p. 1204.

QUANTITATIVE SEPARATIONS OF METALS IN ALKALINE SOLUTIONS BY HYDROGEN PEROXIDE.

By P. JANNASCH and E. v. CLOEDT.

Separation of Bismuth, Lead, and Manganese from Mercury.

1. *Separation of Bismuth from Mercury.*

As an initial point for their experiments the authors used pure metallic bismuth and mercuric oxide. The weighed quantities were heated in a covered porcelain capsule with 10 c.c. of concentrated nitric acid and 50 c.c. of water on the water-bath, until completely dissolved. The liquid is then slowly poured into a mixture of 25 to 30 c.c. of concentrated ammonia, 25 c. c. of hydrogen peroxide at 3 to 4 per cent, and 50 c.c. of water. There ensued a brisk effervescence of escaping oxygen, and the bismuth subsided as a yellowish-grey deposit of hydrated peroxide. It was then dissolved on the filter in dilute hot nitric acid, again precipitated as before, filtered, and weighed in a platinum crucible as bismuth peroxide.

Since for precipitating the bismuth we used hydrogen peroxide purified by distillation *in vacuo*, no correction for silica, alumina, &c., is needed. Still we must advise that the pure hydrogen peroxide should be used as fresh as possible, since its solutions on prolonged standing seem to attack sensitive kinds of glass, and may thus be anew contaminated with silica.

If the first deposit of bismuth is washed with extreme care, a single precipitation is sufficient for accurate separation. We have proved this in a couple of special experiments.

For the determination of the mercury the entire ammoniacal filtrate is evaporated down for the complete expulsion of the excess of ammonia, strongly acidified with sulphurous acid, the liquid poured into a larger beaker, diluted to at least 300 c.c., and lastly precipitated at a moderate heat with sulphuretted hydrogen. The further treatment of the mercury sulphide and its weighing are effected in the usual way.

2. *Separation of Lead and Mercury.*

The separation is effected by pouring the solution of the nitrate, acidified with nitric acid, into the ammoniacal oxidising liquid. The results are very satisfactory. It must be observed that, prior to filtration, the lead precipitate is allowed to stand for some time (thirty minutes to one hour), with occasional stirring, as otherwise traces of lead may remain in solution. The lead hydro-peroxide is filtered off, well washed with cold water, dissolved on the filter in dilute nitric acid (equal to about 10 c.c. of the concentrated acid), with a simultaneous addition of hydrogen peroxide, and precipitated again in the same manner.

3. *Separation of Manganese and Mercury.*

The separation of these metals is effected with great ease, which appears the more remarkable as manganese—in consequence of its tendency, when in the state of peroxide, to carry other oxides down with it—is apt to frustrate the smooth course of an analysis. The authors took, as their initial point, manganese-ammonium sulphate and mercuric oxide. From 0·3 to 0·4 grm. of each substance was dissolved in 50 c.c. water and 10 c.c. of concentrated nitric acid. This mixture is added to a liquid of 30 c.c. hydrogen peroxide, 30 c.c. strong ammonia, and 50 c.c. water. After heating for thirty minutes in a covered beaker on the water-bath, the precipitate is filtered and washed with a mixture of water, ammonia, and hydrogen peroxide, and finally with hot water. The precipitate may be ignited in a platinum or porcelain crucible, either whilst still moist or after a partial drying. The coarser particles are carefully crushed, and the ignition is continued until the weight becomes constant.—*Zeitschrift für Anorganische Chemie.*

ON THE
ABSORPTION-SPECTRUM OF LIQUEFIED AIR.

By Professors **LIVEING** and **DEWAR**.

In a recent conversation on the absorption-spectrum of liquefied oxygen, M. Cornu suggested to us that it would be interesting to examine if the diffused absorption bands would develop as well when the density of oxygen is produced by a reduction of temperature at atmospheric pressure, as when the gas is compressed at higher temperatures.

M. Janssen has found that the intensity of these bands increases as the square of the density of oxygen, and has recently verified this result by observations of the solar spectrum in the desert of Sahara. This law, as we have already pointed out (*Proc. Roy. Soc.*, xlvi., p. 228), seems to indicate that these bands are due either to complex molecules produced by condensation, or to the encounters of molecules of an ordinary mass—encounters which are more frequent when their free path is diminished.

To reply to M. Cornu's question, we obtained liquefied air directly from the atmosphere by the cold due to the rapid evaporation of liquid oxygen under a low pressure. The method and the apparatus have been already described by Prof. Dewar (*Proc. Royal Institution*, xx., January, 1893).

The absorption due to liquefied air of the thickness of 1·9 c.m. was then compared directly with that of liquid oxygen, of the thickness of 0·4 c.m. The light which had traversed this latter medium was introduced, by means of a reflection-prism, into the field of vision of the spectroscope at the same time as that which had traversed the liquid air. The position of the lamps was then regulated so that the brightness of the spectral regions free from bands was the same in the two spectra. Under these conditions it was observed that intensity of the absorption-bands was developed much more by 0·4 c.m. of liquid oxygen than by a depth of liquid air five times greater.

The vessels containing the liquids were open, the liquid air evaporated gradually, and as the boiling-point of nitrogen is below that of oxygen the nitrogen evaporated more rapidly, and the residual liquid contained a greater and greater proportion of oxygen. Therefore the absorption-bands become more and more intense, until they surpassed in intensity that of the slighter depth of oxygen.

Another portion of air liquefied like the former was rapidly mixed with an equal volume of liquid oxygen, and the absorption of this mixture was compared as above with that of liquid oxygen. We recognised that the absorption of 2·4 c.m. of the mixture was much greater than that of 0·4 c.m. of liquid oxygen. The density of the oxygen in this mixture was, in fact, three times greater than that of the oxygen in pure liquefied air, and, according to the law of Janssen, the absorption ought to become nine times greater. Our observations, therefore, agree with this result.

These observations agree also with the theory of the continuity of the liquid and the gaseous states. We must remember that air boils at a temperature lower than does oxygen, so that the two liquids to be compared were not at the same temperature by about 10°.

If the diffused absorption-bands of oxygen are produced by their mutual collisions in the gaseous and liquid states, it is permissible to suppose that they would be profoundly modified if the oxygen assumed the solid state. Hitherto oxygen has not yet been solidified in a state of purity, but liquid air is easily brought to the solid state by rapid evaporation under a low pressure (Dewar, *Proc. Royal Institution*, January 19, 1894).

Whether the solid thus obtained is homogeneous, or merely formed of a paste of solid nitrogen mixed with liquid oxygen, may be open to discussion, but in any case it is beyond doubt that the oxygen is at the lowest temperature which has been attained. Consequently, we have examined if a difference can be perceived between the absorptions of solid and of liquid air. There was no difference in the character of the absorptions, and very little in the intensities.

To gauge the effects of the temperature, we compared the absorption of a depth of 3 c.m. of liquid oxygen, boiling under a pressure of about 1 c.m., with that of an equal depth of the same liquid at the atmospheric pressure. With the coldest liquid, the bands in the orange and the yellow were appreciably elongated, enlarged especially on the more refrangible side. The weak band in the green was darker, and the band in the blue seemed also somewhat stronger. The difference of temperature might be about 17°, which does not seem much, though it is about the fifth part of the temperature of the warmer liquid.—*Comptes Rendus*, cxxi., p. 162.

Examination of Seed-lac.—A. Gascard (*Journal de Pharmacie*).—Cold alcohol at 95 per cent extracts from the lac its most important resinous ingredient, which is important for the varnish manufacture, and is said to be a mixture of several acids of the fatty series, and to contain nitrogen. The portion soluble in boiling alcohol of the same strength separates out on cooling in the form of needles, and has the properties and composition of the waxes. It is a mixture of several esters of myricyl alcohol with more than 50 per cent of free myricyl alcohol.

ON THE SPECTRA OF ARGON.*

By WILLIAM CROOKES, F.R.S., &c.

THROUGH the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train. The results are both interesting and important, and entirely corroborate the conclusions arrived at by the discoverers of argon.

The results of my examination are given in a table of wave-lengths, which follows, and on a map of the lines accurately drawn to scale, accompanying this paper. The map is 40 ft. long, and the probable error of position of any line on it is not greater than 1 m.m.

Argon resembles nitrogen in that it gives two distinct spectra, according to the strength of the induction current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, both the argon spectra consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and however free it was supposed to be from nitrogen, I could always at first detect the nitrogen bands in its spectrum. These, however, soon disappear when the induction spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum tubes best adapted for showing the spectra are of the ordinary Plücker form, having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end. I have also used a Plücker tube made entirely of quartz worked before the oxy-hydrogen blowpipe. I have not yet succeeded in melting platinum or iridio-platinum wire terminals into the quartz, as they melt too easily, but a very good spectrum is obtained by coating the bulbs outside with tinfoil, connected with the terminals of the induction coil.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is 3 m.m. At this point the colour of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wave-lengths 696·56 and 705·64. On passing the current the traces of nitrogen bands disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs owing to what I have called "electrical evaporation,"† and I think the residual nitrogen is occluded by the finely-divided metal. Similar occlusions are frequently noticed by those who work much with vacuum tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the circuit, the colour of the luminous discharge changes from red to a rich steel blue, and the spectrum shows an almost entirely different set of lines. The two spectra, called for brevity red and blue, are shown on the large map, the upper spectrum being that of "blue" argon, and the lower one that of "red" argon. It is not easy to obtain the blue colour and spectrum entirely free from the red. The red is easily got by using a large coil‡ actuated with a current of 3 ampères and 6 volts. There is then no tendency for it to turn blue.

The blue colour may be obtained with the same coil by actuating it with a current of 3·84 ampères and 11 volts, intercalating a jar of 50 square inches surface. The make-and-break must be screwed up so as to vibrate as rapidly as possible. With the small coil a very good blue colour can be obtained by using three Grove cells and a Leyden jar of 120 square inches surface, and a very rapid make-and-break. It appears that an electromotive force of 27,600 volts is required to bring out the red, and a higher E.M.F. and a very hot spark for the blue. It is possible so to adjust the pressure of gas in the tube that a very slight alteration of the strength of the current will cause the colour to change from red to blue, and *vice versa*. I have occasionally had an argon tube in so sensitive a state that with the commutator turned one way the colour was red, and the other way blue. Induction coils actuated by a continuous current are never symmetrical as regards the polarity of the induced current, and any little irregularity in the metallic terminals of the vacuum tube also acts as a valve. The red glow is produced by the positive spark, and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen.* In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow 80 lines, making 199 in all; of these, 26 appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor Ramsay I was allowed to take some vacuum tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminium terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, contaminated by a trace of nitrogen bands. The next day the tube with platinum terminals was unchanged, but that having aluminium terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour's current and a few days' rest the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is submitted to the induced current in a tube made of fused and blown quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum tube was filled with argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8·84 ampères and 11 volts; no jar being interposed. At a pressure of 3 m.m. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until at a pressure of about half a m.m. flashes of blue light made their appearance. At a quarter of a m.m. the colour of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

A striking instance of a change of spectrum from nitrogen to argon was shown in a tube filled with argon kindly sent me by Lord Rayleigh. It had been prepared from the atmosphere by sparking, and it was considered to contain about 3 per cent of nitrogen. This argon was passed into an exhausted tube and then rarefied to a pressure of 75 m.m. and kept on the pump. At this pressure the nitrogen conducted all the induction current, the spectrum showing nothing but the nitrogen bands. The pump was slowly kept going, and spectrum observations were continuously taken. When the pressure fell to about 3 m.m. a change came over the spectrum, the nitrogen bands disappeared, and the spectrum of argon took its place; the only contamination being a little aqueous vapour, due to my not having sufficiently dried the gas. I took photographs of the spectrum given by this tube in the two stages, one show-

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[*] From the *Philosophical Transactions of the Royal Society*, vol. clxxxvi. (1895), A., pp. 243-251.

[†] *Roy. Soc. Proc.*, vol. l, p. 88, June, 1891.

[‡] The coil used has about sixty miles of secondary wire, and when fully charged gives a torrent of sparks 24 inches long. The smaller coil gives six-inch sparks when worked with six half-pint Grove cells.

[*] Photographs of the different spectra of argon, and other gaseous spectra for comparison, were projected on the screen.

ing the pure nitrogen bands and the other the argon lines, each being compared with the spectrum of argon prepared by Professor Ramsay. Observations have shown that the spectra given by argon, obtained by the sparking method of Lord Rayleigh and by the magnesium method of Prof. Ramsay from the atmosphere, are identical.

It was of interest to see how little argon could be detected in admixture with nitrogen by combined pumping and passage of the current. Some argon prepared by myself,* having 60 to 70 per cent of nitrogen with it, was put into a small tube furnished with large platinum terminals. Exhaustion was carried to 3 m.m., and the tube was then sealed off. The spark from the large coil actuated with a current of 3·84 ampères and 11 volts was then put on, and the spectrum examined continuously. At first it showed only the nitrogen bands. In about half an hour the nitrogen began to fade and the argon lines appear, and in a few minutes later the tube was just short of non-conducting, the colour of the gas was rich steel-blue, and the spectrum was that of the blue argon glow. Here the small diameter of the bulbs of the tube and the large platinum wires facilitated much spattering or "electrical evaporation" of the platinum. The pressure also was the one most suitable for that phenomenon. To this I attribute the rapid occlusion of the residual nitrogen.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of 52 m.m. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction current from the large coil for eight hours before any change was noticed. The last time I used it for photographing the nitrogen spectrum difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The colour immediately changed from the reddish yellow of nitrogen to the blue of argon, and on applying the spectroscope the lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty and by employing a very small jar I was able to take one photograph of this changed spectrum and compare it with the spectrum of argon from Professor Ramsay, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through, except by employing a dangerously large current. Whenever a flash passed it was of a deep blue colour. Assuming that the atmosphere contains 1 per cent of argon, the 3 m.m. of nitrogen originally in the tube would contain 0·03 m.m. of argon. After the nitrogen had been occluded by the spattered platinum, this pressure of argon would be near the point of non-conduction.

In all cases when argon has been obtained in this manner the spectrum has been that of the blue-glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark: partly also on the degree of exhaustion. Nitrogen, when present, conducts the current easiest. As the exhaustion increases and the conductivity of the nitrogen diminishes, that of the red-glowing argon rises, until at a pressure of about 3 m.m. its conductivity is at the greatest and the luminosity is best. Beyond that point the conductivity of the red form seems to get less, and that of the blue form to increase, till the vacuum approaches a fraction of a m.m., when further pumping soon renders it non-conducting. It is not improbable, and I understand that independent observations have already led both the discoverers to the same conclusion—that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum tubes containing rarefied nitrogen which show either the fluted band or the sharp line spectrum by simply turning the screw of the make-and-break: exactly as the two spectra of argon can be changed from one to the other.

The disappearance of the red glow and the appearance of the blue glow in argon as the exhaustion increases also resembles the disappearance of the red line of hydrogen when exhaustion is raised to a high point. Plücker, who was the first to observe this occurrence, says*: "When Ruhmkorff's small induction coil was discharged through a spectral tube enclosing hydrogen, which was gradually rarefied to the highest tenuity to be reached by means of Geissler's exhauster, finally the beautiful red colour of the ignited gas became fainter, and passed gradually into an undetermined violet. When analysed by the prism, Hα (the red, C, line) disappeared, while Hβ (the green, F, line), though fainter, remained well defined. Accordingly, light of a greater length of wave was the first extinguished."

The line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed shows that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at 531·7, the aurora line at 557·1, and the helium line at 587·5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapour yield spectra at all like those of argon, and the apparent coincidences in some of the lines, which, on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. Having once obtained a tube of argon giving the pure spectra, I can make no alteration in it except that which takes place on varying the spark or increasing the exhaustion, when the two spectra change from one to the other. As far, therefore, as spectrum work can decide, the verdict must be that Lord Rayleigh and Professor Ramsay have added one, if not two, members to the family of elementary bodies.

Blue.		Red.	
Wave-length.	Intensity.	Wave-length.	Intensity.
		764·6	2
		750·6	4
		737·7	3
		726·3	2
		705·64	10
		696·56	9
		684·2	2
		675·4	6
		666·4	6

---

* When a current of 65 volts and 15 ampères alternating 130 times a second is passed through the primary of my large coil, an arching flame, consisting of burning nitrogen, issues from each of the secondary poles, meeting in the middle. When once started the poles can be drawn asunder, till the flame bridges across 212 m.m. When the terminals are more than 46 m.m. apart the flame will not strike across. By enclosing this flame in a reservoir over alkaline water, and feeding it with air and oxygen, I can burn up a litre of air an hour.

* "On the Spectra of Ignited Gases and Vapours," by Drs. Plücker and Hittorf, *Phil. Trans.*, Part 1, clv., p. 21.

BLUE.		RED.		
Wave-length.	Intensity.	Wave-length.	Intensity.	
662·8	4			
		640·7	9	
		637·7	2	
		630·2	4	
		628·1	2	
623·2	4			
		621·0	6	
617·3	6	617·3	6	Coincident.
		614·3	2	
612·0	6			
		609·9	4	
		605·6	2	
		604·5	3	
603·8	8	603·8	8	Coincident.
		593·5	1	
592·6	4	592·6	4	Coincident,
		590·9	6	
		588·7	6	
		585·8	4	
		583·4	2	
		580·3	1	
		577·1	2	
		574·6	6	
		568·3	2	
		565·1	9	
		561·0	9	
		556·7	2	
		555·7	10	
		552·0	1	
		550·1	2	
		549·65	8	
		545·6	6	
		544·4	2	
		542·1	4	
		525·8	6	
		522·2	7	
		518·58	10	
		516·5	9	
514·0	10			
506·5	10	506·5	4	Coincident.
501·2	2	501·2	4	Coincident.
500·7	9			
496·55	9	496·55	4	Coincident.
493·8	10	493·8	2	Coincident.
487·9	10	487·9	4	Coincident.
484·75	1			
480·50	7			
476·30	1			
473·45	6			
472·66	2			
		470·12	8	
465·65	5			
		462·95	5	
460·80	8			
		459·45	2	
458·69	6			
457·95	6			
454·35	7			
		451·40	2	
450·95	8	450·95	9	Coincident.
447·83	6			
442·65	10			
442·25	10			
439·95	10			
437·65	9			
436·90	9			
434·85	10			
		434·50	5	
433·35	9	433·35	9	Coincident.
		430·05	9	
429 90	9			
427·70	3			
427·20	7	427·20	8	Coincident.
426·60	6	426·60	4	Coincident.
425·95	8	425·95	9	Coincident.
425·15	2	425·15	3	Coincident.
422·85	6			
420·10	10	420·10	10	Coincident.
419·80	9	419·80	9	Coincident.
419·15	9	419·15	9	Coincident.
418·30	8	418·30	8	Coincident.
416·45	8	416·45	4	Coincident.
415·95	10	415·95	10	Coincident.
		415·65	6	
413·15	3			
410·50	8			
407·25	8			
404·40	8	404·40	9	Coincident.
403·30	1			
401·30	8			
397·85	1			
396·78	3			
394·85	9	394·85	10	Coincident.
394·35	3			
393·18	3			
392·85	9			
392·75	3			
391·50	1			
		390·45	8	
389·20	5			
387·55	2			
387·18	2			
386·85	8			
385·15	10			
384·55	1			
383·55	2	383·55	3	Coincident.
382·75	2			
380·95	4			
380·35	1			
379·95	1			
378·08	9			
		377·15	1	
377·05	2			
376·60	8			
373·85	3			
372·98	10			
371·80	4			
		363·25	2	
363·17	1			
		362·37	1	
		362·28	1	
361·75	2			
360·50	3	360·50	5	Coincident.
358·70	10			
358·03	9			
357·50	9			
356·65	2	356·65	4	Coincident.
356·40	2			
		356·28	1	
356·00	2			
355·82	7			
355·45	4	355·45	6	Coincident.
354·75	4			
354·45	7			
353·43	4			
352·05	3			
351·92	4			
351·35	6			
350·88	4			
349·00	10			
347·57	7			
345·35	1			
338·80	1			
309·27	5			
308·48	4			
306·47	2			

Blue.	
Wave-length.	Intensity.
304·27	3
299·82	1
297·86	1
294·27	2
292·96	1
283·02	1
279·44	2
273·45	2
270·72	0·5
269·30	1
266·12	2
265·26	3
262·95	1
257·12	2
256·07	1
248·49	1
243·85	2
224·66	3

119 lines in the "Blue" spectrum.
80 lines in the "Red" spectrum.

199 total lines.
26 lines common to the two spectra.

CHROMATES OF THE RARE EARTHS: CHROMATES OF THORIUM.

By CHASE PALMER.

Believing that a study of the action of an acid of feeble energy upon the weak bases of the tin group—or Fourth Group of Mendeleeff's Periodic System—would throw new light upon this interesting family of elements, I have undertaken a comparative study of the action of chromic acid upon the oxides of the rarer metals of this group, and of the conduct of their salts towards the alkaline chromates.

The chromates of the rare elements of this group have hitherto received but little attention from chemists. The earliest allusion to a chromate of a rare earth was made in 1863 by J. J. Chydenius ("Thorerde und deren Verbindungen," *Ann. der Phys. Pogg.*, cxix., 43). This author observes that thorium hydroxide is soluble in chromic acid. He states that from the resulting solution, evaporated over sulphuric acid, he obtained normal thorium chromate as a soluble salt containing eight molecules of water of crystallisation. Chydenius further states that potassium dichromate produces no precipitate when added to a solution of thorium chloride, until after the mixture is neutralised with ammonia, whereby a basic salt of thorium is thrown down. The only other allusion to a chromate of a rare metal of the Fourth group, in the literature accessible to me, is made by Pattison and Clarke (Chem. News, xvi., 259). These chemists observed that by heating the residue from an evaporated solution of the hydroxides of cerium, lanthanum, and didymium in chromic acid, the cerium compound was rendered insoluble; but there is no evidence that they determined the composition of the insoluble product.

Thorium was chosen as the first element for the present research on account of the highly developed basic properties of its oxide. Contrary to the observations of Chydenius, I have found, not only that a difficultly soluble salt, having the composition of normal thorium chromate, separates spontaneously from a solution of thorium hydroxide in chromic acid, but also that the same compound is precipitated by potassium dichromate from thorium nitrate without the aid of a neutralising alkali. I have also found that potassium chromate produces the same compound indirectly from a soluble thorium salt.

Thorium Hydroxide and Chromic Acid.—Pure freshly precipitated thorium hydroxide was added in portions to a solution of pure chromium trioxide in water. The quantity of the trioxide was slightly in excess of the amount required to form the normal chromate. The hydroxide was quickly dissolved at first, but afterwards the acid attacked it more sluggishly. A flocculent orange precipitate soon appeared, and finally settled as a fine powder. Under the microscope this product shows a crystalline structure. The formation of the orange precipitate takes place more quickly at 90° C. than at the ordinary temperature.

Dried at 120° C. to constant weight the product was analysed:—

0·2016 grm. substance at 180° lost 0·0072 grm. H_2O and gave 0·1114 grm. ThO_2 and 0·0626 grm. Cr_2O_3.

	Calculated for $Th(CrO_4)_2.H_2O$.	Found.
H_2O	3·73	3·57
Th	48·05	48·55
Cr	21·71	21·29

Thorium Chromate from Chromic Acid Solution.—Pure freshly-precipitated thorium hydroxide, in small portions at a time, was stirred in a cold solution of chromic acid as long as it was taken up. At the first appearance of the orange precipitate, the latter was filtered off, and the solution evaporated over sulphuric acid *in vacuo*. From the concentrated solution thorium chromate separated out in orange-coloured scales containing two molecules of water of crystallisation and one molecule of water of constitution.

Dried to constant weight over sulphuric acid the salt was analysed.

I. 0·215 grm. substance lost 0·0148 grm. H_2O at 120°; at 180° it lost 0·007 grm. H_2O additional, and gave 0·1104 grm. ThO_2 and 0·0631 grm. Cr_2O_3.

II. 0·2155 grm. substance lost 0·015 grm. H_2O at 120°; at 180° it lost 0·0068 grm. H_2O additional, and gave 0·111 grm. ThO_2 and 0·0622 grm. Cr_2O_3.

	Calculated for $Th(CrO_4)_2.3H_2O$.	Found. I.	Found. II.
$2H_2O$	6·90	6·88	6·96
H_2O	3·46	3·25	3·15
Th	44·71	45·12	45·26
Cr	20·20	20·12	19·70

Thorium Nitrate and Potassium Dichromate.—On mixing the boiling solutions of these salts in the proportion of one molecule of the nitrate to two molecules of the dichromate, hydrated thorium chromate was precipitated at once as a fine orange powder. In this way 78 per cent of the theoretical yield was obtained.

0·1986 grm. substance, dried at 120°, lost 0·0073 grm. H_2O at 180° and gave 0·1095 grm. ThO_2 and 0·0068 grm. Cr_2O_3.

	Found.
H_2O	3·67
Th	48·35
Cr	21·34

When the cold solutions of thorium nitrate and potassium dichromate were mixed no immediate precipitation occurred, but in a short time a precipitate began to form. After standing twenty-four hours the orange precipitate that had formed meanwhile was filtered off, washed, and dried at 120°.

0·1817 grm. substance lost 0·0064 grm. H_2O at 180°, and gave 0·1008 grm. ThO_2 and 0·0569 grm. Cr_2O_3.

	Found.
H_2O	3·52
Th	48·75
Cr	21·47

The filtrate from this precipitate was heated to 90°. At 60° a second precipitation of the thorium chromate occurred. The first yield was 65 per cent, and 14 per cent additional was obtained by heating the filtrate. The total yield (79 per cent) closely corresponds with the yield obtained by precipitating the compound at once from a boiling solution.

The mother-liquor from the second precipitate was reduced to small volume, but no further precipitation occurred. By evaporating it to dryness a very soluble crystalline product was left, but it could not be isolated for examination.

Thorium Nitrate and Potassium Chromate.—There are two stages in the formation of hydrated thorium chromate from thorium nitrate and potassium chromate. When a solution of thorium nitrate is treated with a solution of potassium chromate (one molecule of the former to three molecules of the latter), the precipitate, which at once forms, dissolves immediately until the mixture is complete. Then a dense golden yellow precipitate separates from the solution. The liquid meanwhile becomes red, owing to the formation of potassium dichromate. By promptly removing the yellow precipitate from contact with the fluid it was found, on analysis, to be basic thorium chromate.

0·2367 grm. substance dried at 100° gave 0·1635 grm. ThO_2 and 0·0459 grm. Cr_2O_3.

	Calculated for $Th(OH)_2CrO_4$.	Found.
Th	60·66	60·70
Cr	13·70	13·29

If the basic thorium chromate be allowed to remain in contact with the supernatant liquid, it is gradually changed into the orange precipitate, which, upon analysis, proved itself to be the same hydrated thorium chromate already described. During this transformation the red liquid is changed to the bright yellow colour of potassium chromate.

Analysis of the final product dried at 120°:—

0·2136 grm. substance at 180° lost 0·0081 grm. H_2O and gave 0·1175 grm. ThO_2 and 0·0678 grm. Cr_2O_3.

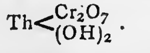
	Found.
H_2O	3·79
Th	48·34
Cr	21·77

The complete reaction may be expressed by the two equations:—

1. $Th(NO_3)_4+3K_2CrO_4+H_2O= =Th(OH)_2CrO_4+K_2Cr_2O_7+4KNO_3$.
2. $Th(OH)_2CrO_4+K_2Cr_2O_7=Th(CrO_4)_2.H_2O+K_2CrO_4$.

The hydrated thorium chromate always has a full orange colour, which it does not lose even after prolonged heating at 130°. The colour of the anhydrous salt is ochreous yellow. At 22°, 1 part of the salt is soluble in 284 parts of water. It is readily soluble in hydrochloric acid and in ammonium carbonate. At a dull red heat it is decomposed into thorium dioxide and chromic oxide. Heated in a platinum crucible over a Bunsen lamp the substance lost 10·41 per cent in weight. For the loss of three oxygen atoms to form ThO_2 and Cr_2O_3 the required loss in weight is 10·32 per cent.

Constitution of the Orange Chromate—It is noteworthy that the orange chromate of thorium always contains one molecule of firmly bound water, whether the substance be formed by slow crystallisation from a chromic acid solution, or by precipitation from a soluble salt, or formed from the insoluble basic chromate. The substance may be regarded simply as hydrated normal thorium chromate, $Th(CrO_4)_2H_2O$, or it may be a basic dichromate of thorium having the constitution expressed by the formula



$$Th<^{Cr_2O_7}_{(OH)_2}.$$

Before expressing an opinion as to the more probable constitution of the orange chromate, I shall attempt to gather more knowledge of these chromates and of the compounds of chromic acid with the related elements.

Zirconium hydroxide is attacked by chromic acid less readily than is thorium hydroxide. It can be completely dissolved in an excess of the acid. A yellow precipitate was obtained by boiling this solution. From an analysis, the product appears to be a basic salt.

A similar yellow precipitate is obtained by the action of potassium dichromate on zirconium chloride. The precipitate, dried over sulphuric acid, gave 41·24 per cent Zr and 16·38 per cent Cr. It is probably a basic salt.

I intend to make a thorough study of the chromates of zirconium and of the other elements of the Fourth Group.

I wish to express here my hearty thanks to Professor Edgar F. Smith, through whose generous hospitality I have enjoyed the facilities of the John Harrison Chemical Laboratory of the University of Pennsylvania, where the work described in this paper has been done.—*American Chemical Journal*, xvii., No. 5.

THE WET ASSAY FOR COPPER.

By R. S. DULIN.

It seems difficult for the metallurgical chemists of this country to settle upon a uniform method for the rapid determination of copper. We should have a standard method, applicable for all commercial work, which would be fairly accurate under as many possible varying conditions, so that results obtained from the same ore, by different chemists, should be substantially uniform. For about nine months past I have been engaged upon an extended series of experiments, having for their object a determination of the chief causes for variation and error in the methods most generally employed, and for the purpose of finding a modification of common methods which would be an improvement upon those now used. At the same time I have made myself conversant with much of the current literature upon the subject, and the observations herein offered, while based upon my individual experiments, are corroborated, in most part, by the published results of others.

There are at present three well-recognised methods employed in the United States for the determination of copper. Each method has its own advocates, and it is perfectly fair to say that either method, in the hands of a skilled chemist, thoroughly understanding the reactions of the methods, working with all due care, will yield substantially the same results. The methods referred to are:—

1. The cyanide method. 2. The iodide. 3. The electrolytic. A colorimetric method is also employed for the determination of copper when the percentages fall below 2 per cent. I have made no particular study of this method, and, as it is only employed in special cases, I shall make no further reference to it.

The cyanide method depends upon the fact that, when a solution of potassium cyanide is run into an ammoniacal solution of copper, the blue colour is discharged. The reaction is as follows:—

$$(NH_4)_2(NH_3)_2,CuO(NO_3)_2+4KCN+3H_2O= =K_2Cu(CN)_4+2KNO_3+4NH_4OH.$$

This method is fully described in Furman's "Manual of Practical Assaying." The following precautions should always be carefully observed:—1. The bulk of the liquid titrated should always be uniform; by inattention to this an error of from 2 to 3 per cent is possible. 2. The solution should always be cooled to the temperature of the laboratory before titrating, otherwise an error of about 3 per cent is possible. 3. The amount of ammonia added should be nearly constant, otherwise the possible error may amount to as much as 5 per cent, or even more.

These precautions are general, and must always be carefully observed in every modification which may be made in the method. In the ordinary modification of the method, ferric hydroxide is almost certain to be precipitated upon the addition of the ammonium hydroxide. If the amount be small, no error is apt to occur, but it should always be filtered off. If the amount be large, it is not easy to wash out all of the copper salt, thereby causing lower results, unless large quantities of wash-water are employed, thus increasing and varying the bulk. The error arising from increased bulk may be obviated, by taking, after mixing, an aliquot part of the solution; if the solution be not thereby made very dilute the error is so slight that it may be neglected. If salts of manganese are present the end reaction cannot be determined, owing to the liquid first turning green, finally black. The presence of large quantities of calcium, I found, confused the end reaction, causing error of importance. Experiments made showed that magnesia did not interfere, and the presence of antimony and arsenic was found to cause no sensible variations.

Zinc, which is almost certain to be present in varying amount, is a possible source of great error. The following results were obtained from a large number of carefully conducted experiments. Only the averages are given, and they are substantially the same as the extremes. In these experiments the bulk of the liquid varied from 25 to as much as 50 c.c., thereby causing a slight error, for which no correction has been made. This error would not substantially change the results. Careful attention was paid to the precautions previously enumerated.

Weight of copper.	Weight of zinc.	Cyanide used.	Increase.
0·05	0·00	10·4 c.c.	—
0·05	0·01	11·0 ,,	0·6 c.c.
0·05	0·02	11·7 ,,	1·3 ,,
0·05	0·03	12·3 ,,	1·9 ,,
0·05	0·04	12·9 ,,	2·5 ,,
0·05	0·05	14·0 ,,	3·6 ,,
0·05	0·06	16·1 ,,	5·7 ,,
0·05	0·07	18·9 ,,	8·5 ,,
0·05	0·08	21·6 ,,	11·2 ,,
0·05	0·09	24·3 ,,	13·9 ,,

These results show that there is a gradual increase of about six-tenths c.c. in the amount of the cyanide solution required, until the amount of zinc present nearly equals the amount of copper, when the increase becomes variable, until the amount of zinc becomes greater than the amount of copper to the extent of 20 per cent, when the increase, though larger, about $2\frac{7}{10}$ c.c., again becomes regular.

The effects of cadmium are similar, as shown by the following results, which are also the averages of a large number of experiments, in which the extremes are farther removed from the mean than was found with zinc. As in the preceding experiments, the precautions previously enumerated were very carefully observed, except in the case of bulk, in which the variations were identically the same as with the experiments with zinc.

Weight of copper.	Weight of cadmium.	Cyanide used.	Increase.
0·05	0·00	10·4 c.c	—
0·05	0·01	10·6 ,,	0·2 c.c.
0·05	0·02	10·8 ,,	0·4 ,,
0·05	0·03	11·1 ,,	0·7 ,,
0·05	0·04	11·6 ,,	1·2 ,,
0·05	0·05	12·0 ,,	1·6 ,,
0·05	0·06	12·4 ,,	2·0 ,,
0·05	0·07	13·5 ,,	3·1 ,,
0·05	0·08	14·5 ,,	4·1 ,,

These results show that there is a gradually accumulating increase in the consumption of cyanide due to the presence of cadmium. As cadmium is a constituent usually found associated with copper, it must be removed if reliable results be required. Silver also interferes, but in a regular way. If the amount of silver be known, by previous assay, it is best allowed for by calculation.

The following modification of the cyanide method has been thoroughly tested, under the immediate supervision of Prof. Seamon, and it is recommended as giving results equal in value to those obtained by the electrolytic method.

The ore is treated according to the method described on page 161 of Furman's "Manual of Assaying." In this way a solution of the copper salt is obtained, practically free from lead and silver. This solution is boiled with strips of aluminum foil, resulting in the complete precipitation of the copper together with any silver which may remain in the solution, which is always so small as to be negligible, as I have demonstrated by a number of experiments upon different ores. If cadmium be present it is only partially precipitated, beginning after the copper is thrown down. If care be taken to stop the boiling, immediately after the copper is precipitated, which can be determined with constant practice by the eye, the amount of cadmium precipitated is so small as not to cause sensible error. The liquid is decanted from off the aluminum foil and copper, quickly washed several times with hot water, care being taken not to wash away any particles of the copper; 3 c.c. of nitric acid are then added to the flask, and boiled to dissolve the copper; the solution is then treated with ammonium hydroxide as in the usual way, and titration is made with the usual solution of cyanide.

This method has been very carefully tested, and the results were so satisfactory, and nearly uniform, that I recommend it as being as accurate as the electrolytic method, under the conditions in which the latter is usually employed.

The iodide method is most commonly employed in the Lake Superior District and in foreign countries, where it is regarded with much favour. Many chemists regard it as more accurate than the cyanide or electrolytic methods, and there is no doubt from my experiments that it is more accurate than the ordinary modification of the cyanide and equal to that of the electrolytic. The method depends upon the following reactions:—

$$2CuSO_4+4KI=Cu_2I_2+2I+2K_2SO_4$$
$$2Na_2S_2O_3+2I=2NaI+Na_2S_4O_6.$$

The best results are obtained when the copper is precipitated with aluminum foil, as previously described under the cyanide method. The method is fully described in Furman's "Manual of Assaying," and I only desire to call attention to the necessity for attending to the following precautions:—

1. The presence of iron in about equal amounts with the copper requires more "hypo," increasing the amount of copper to the extent of 2 to 3 per cent. 2. The solution should be titrated cold. 3. The presence of large amounts of alkaline salts, particularly sodium sulphate, decreases the amount of copper. 4. The presence of bismuth clouds the end reactions. My experience with the modification of this method, in which the copper is first precipitated with aluminum foil, convinces me that with this change the results are as accurate as those obtained with the modified cyanide method; but it is not so rapid, owing to the time lost at various stages: this is an important factor in the adoption of any method for metallurgical work, when thirty and forty assays must be completed every day. The method is a little more difficult to manipulate than the cyanide method.

The electrolytic method is perhaps the most highly favoured in this country. It has the reputation for greatest accuracy. It requires more time than either of the other; but since it is easy to regulate the work, so that the battery will precipitate during the night, this is not of so much importance. In regular routine work, after solution is effected, the copper should be precipitated with hydrogen sulphide, otherwise many interfering metals are apt to be present and deposited with the copper. I have found that errors from this source are largely, if not entirely, eliminated, if deposition be made from a solution containing a large amount of nitric acid. My best results were obtained when I added 20 c.c. of strong nitric to about 150 c.c. of solution. This holds up the other metals, but a stronger current is required to precipitate all of the copper, and more attention must be paid to proper and rapid manipulation after precipitation. This method is much improved by previously precipitating the copper from its solution by boiling with aluminum foil and then re-dissolving the copper in nitric acid. The following results, obtained from the same sample, carefully prepared, obtained by the three methods, furnish a fair idea of the relative values of the several methods.

A copper matte, containing 20·15 per cent of copper, as determined by a large number of analyses, made by several different assayers and by different methods, was run by each method. The amount of copper in the second matte, determined from the same data, was found to be 28 per cent, while the per cent of copper in the ore was 30·18.

The results obtained by the cyanide method were respectively 20·15, 27·95, and 30·20 per cent. The copper was first precipitated with the aluminum foil. The same substances, with the iodide method, first precipitating with aluminum foil, gave, respectively, 20·25, 28·35, and 30·3 per cent. By the electrolytic method the same substances gave, respectively, 20·045, 28·15, and 30·05 per cent.

These results justify the statement that the iodide method, with the aluminum modification, gives results usually one-tenth to three-tenths per cent too high, while the electrolytic method is too high or too low, according to the amount of metallic substances present precipitable by the electric current; and the cyanide method gives results which are practically correct.—*Journal of the American Chemical Society*, xvii., p. 346.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

First Paper: The Analysis of Strontic Bromide.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 56).

Ratio of Argentic to Strontic Bromide.

In many of the preceding determinations the bromide of silver resulting from the decomposition was weighed.

Ratio of Strontic and Argentic Bromides.

No. of Anal.	No. of Spec.	Weight of Strontic Bromide taken.	Weight of fused Argentic Bromide found.	Ratio $\frac{SrBr_2}{2AgBr}$	At. wt. of Strontium.
		First Series.			
		Grms.	Grms.		
13.	I.	1·6086	2·4415	65·886	87·669
14.	II.	1·8817	2·8561	65·884	87·662
15.	III.	4·5681	6·9337	65·883	87·657
		8·0584	12·2313	65·8834	87·660
		Second Series.			
16.	III.	1·49962	2·27625	65·881	87·652
17.	III.	2·41225	3·66140	65·883	87·660
18.	III.	2·56153	3·88776	65·887	87·674
19.	V.	6 15663	9·34497	65·882	87·654
		12·63003	19·17038	65·883	87·659

In every case a slight excess of silver nitrate was added, to render the argentic bromide wholly insoluble in the filtrate. The very slight amount which may have been dissolved by the wash water during its brief contact with the precipitate was not considered. The precipitate was collected upon a Gooch crucible; and the traces (0·04 to 0·2 m.grm.) of asbestos carried through were collected upon a small washed filter, ignited separately, weighed, and added to the gain in weight of the crucible. From this was subtracted the loss in weight of the precipitate upon fusion in a covered porcelain crucible. A description of the dark room used for the experiments, and many other precautions and details, will be found in other papers (*Proc. Amer. Acad.*, xxviii., 24; xxxix., 74). The results are tabulated below.

It remains only to bring together the results into one table.

Final Averages.

Oxygen = 16·000.

			Strontium equals
I.	$2Ag : SrBr_2$	First Series	87·644
II.	,, ,,	Second Series	87·663
III.	,, ,,	Third Series	87·668
IV.	$2AgBr : SrBr_2$	First Series	87·660
V.	,, ,,	Second Series	87·659

Total average .. .. .. =87·659
Average, rejecting I. above =87·663

The last average is probably most nearly correct.

The analysis of strontic chloride has already been begun, and the preliminary results indicate that the results given above are certainly not too high. For the present, then, the atomic weight of strontium may be taken as 87·66 if oxygen is 16·00, 87·44 if oxygen is 15·96, and 87·01 if oxygen is 15·88.

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* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*.

NOTICES OF BOOKS.

A Text-Book of the Science and Art of Bread-Making, including the Chemistry and Analytical and Practical Testing of Wheat, Flour, and other Materials used in Baking. By William Jago, F.I.C., F.C.S., Chemist to the National Association of Master Bakers and Confectioners of Great Britain and Ireland; Honorary Consultative Examiner in Bread-Making to the City and Guilds of London Institute for the Advancement of Technical Education; Cantor Lecturer on "Modern Developments of Bread-Making" to the Society of Arts, London, &c. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1895. 8vo., pp. 648.

The baker holds a position essentially distinct from that, *e.g.*, of the grocer, draper, &c. He does not merely buy in the wholesale market and sell by retail; he obtains raw material and supplies it to his customers after it has undergone changes necessary to its general use as food. Hence he has not merely to make a judicious selection of raw materials, but to carry out the changes involved in the conversion of flour into bread.

To effect these changes successfully and economically he must have acquaintances with certain principles, mainly chemical, micro-biological, and physical. Without such knowledge he may certainly, by rule-of-thumb, turn out good bread from January to December; but he is at the mercy of accidents. An unusual sample of flour or of yeast may any day show him to his cost that he is not master of the situation.

The adulteration of flour is judiciously dealt with; but we see here nothing to shake our belief that the intentional sophistication of flour and breads is less prevalent than it was formerly.

The remarks on aluminous baking-powders (p. 489) convince us that, as long as our Courts tolerate quibbling in defence of frauds, Britain will not for some time witness the complete extirpation of sophistication.

Perhaps the presence of the seeds of corn-cockle, darnel, ergot, &c., in flour, is more apt to occur than that of any adulterant purposely added. Due attention is here called to the examination of yeasts by microscopic and biological tests.

The author shows that, contrary to what may be almost called a superstition, white bread is more nutritious than the so-called whole-meal breads. The reason of this is that bran contains no gluten. Whole-meal bread, further, by the irritating action of the bran, accelerates the peristaltic movement of the bowel. Hence an excess of unutilised nitrogenous matter is found in the excreta of persons who have been fed on brown breads. The irritation of the bran may occasion unpleasant, and even dangerous, diarrhœa.

Mr. Jago dwells, in a very instructive and convincing manner, on the sanitary defects of urban bakeries,—on their underground situation, their defective ventilation, their frequent proximity to privies and other sources of nuisance. Nor does he forget to show the importance of kneading by machinery in place of hand-labour, which involves certain features most unappetising and possibly anti-sanitary. In the interest alike of the consumer and the working-baker, underground bakeries and hand-labour in kneading should be superseded. In these days of gas-engines, and of the electric transmission of power, this can be done without burdening the master-baker.

Mr. Jago's work is the more welcome because alien bakers succeed in finding a footing in this country—a fact unpleasant to all who believe in the good old principle "Britain for the British," and especially to all who have had the opportunity of closely observing Continental nastiness as existing in most countries except Holland.

We hope that the "Text-book of the Science and Art of Bread-Making" will be widely circulated and carefully studied."

CHEMICAL NOTICES FROM FOREIGN SOURCES

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 3, July 15, 1895.

Nominations.—As correspondent of the Section of Anatomy and Zoology, Sir William Flower was elected, *vice* Prof. van Beneden. Prof. Ramsay was elected a correspondent for the Section of Chemistry, *vice* Dr. E. Frankland. Singularly enough, Prof. Mendeleeff received only one vote.

Deposit of Aluminium and Potassium Phosphate, and on the Genesis of these Minerals found in Algeria.—Ad. Carnot.—The deposit in question is found in the territory of Misserghin, near Tour Combes. It is found in a cavern of no considerable extent. It contains: Phosphoric acid, 35·17; alumina, 18·18; potassa, 5·80; ammonia, 0·48; lime, 0·31; silica, 11·60; water, with a little organic matter, volatile at 100°, 13·40; do. 100—180°, 10·55; do. at redness, 4·35°; magnesia, fluorine, chlorine, sulphuric acid, traces; total, 99·84. All the facts observed may be explained by the infiltrations of water.

Absorption-spectrum of Liquefied Air.—Professors Liveing and Dewar.—(See p. 65).

Action of the Infra-red Rays upon Silver Sulphide.—H. Rigollot.—This paper will be inserted in full.

Detection and the Presence of Laccase in Plants—G. Bertrand.—The author has discovered laccase in beetroot, carrots, and turnips, in the tubers of dahlia and potatoes, in asparagus, in lucerne, trefoil, rye-grass, in plums, pears, quinces, and chestnuts, and in the flower of the gardenia.

Essence of Linalöe.—Ph. Barbier and L. Bouveault. — The essence in question contains diatomic and tetratomic terpenes, methylheptenone, licareol, licarhodol, and sesquiterpene.

MISCELLANEOUS.

Distinction between Coniin and Nicotin.—G. Heut (*Archiv. der Pharmacie*).—These substances behave differently with phenolphthalein. If we add to nicotin, dissolved in dilute alcohol of 0·95 to 0·96 sp. gr., a drop of a saturated solution of phenolphthalein, the liquid is not coloured red, as it is at once in case of coniin.

The German Association of Naturalists and Physicians.—We learn that the 67th Congress of this Association will be held at Lübeck from September 16th to 23rd. Scientific and medical men of all nations are invited, but the proceedings will be conducted exclusively in the German language. The subjects treated of are resolved into two main groups, that of the natural sciences and that of medicine. The former resolves itself into three subordinate groups. The first of these includes the sections for mathematics, astronomy, physics, chemistry, agricultural chemistry, agricultural experiments, and the lore of instruments. The second comprises the sections for mineralogy, botany, zoology, anthropology, and geography. In the third group are the sections for instruction in mathematics and natural science. A great advantage of the German Association is that it is not encumbered with a section for political economy, a subject for which there is ample scope elsewhere.

Australasian Association for the Advancement of Science.—The Seventh Session of the above Association will be held in Sydney, from the 3rd to the 10th January, 1897, under the Presidency of A. Liversidge, M.A., F.R.S., Professor of Chemistry, University of Sydney. The Presidents and Secretaries of the Sections are as follows:—

Astronomy, Mathematics, and Physics.—R. L. J. Ellery, C.M.G., F.R.S., Government Astronomer, Vict., President; R. Threlfall, M.A., Professor of Physics, and J. Arthur Pollock, B.Sc., Demonstrator in Physics, Sydney University, Secretaries.

Chemistry.—T. C. Cloud, A.R.S.M., F.C.S., Manager Wallaroo Copper Works, South Australia, President; W. M. Hamlet, F.C.S., F.I.C., Government Analyst, N.S.W., Secretary.

Geology and Mineralogy.—Captain F. W. Hutton, M.A., F.R.S., F.G.S., Director of Canterbury Museum, and Lecturer in Geology, Christ Church, New Zealand, President; T. W. E. David, B.A., F.G.S., Professor of Geology and Physical Geography, Sydney University, and E. F. Pittman, A.R.S.M., F.G.S., L.S., Government Geologist, N.S.W., and Lecturer in Mining, Sydney University, Secretaries.

Biology.— T. J. Parker, B.Sc., F.R.S., Professor of Biology, Otago University, Dunedin, New Zealand, President; W. A. Haswell, M.A., D.Sc., F.L.S., Professor of Biology, Sydney University, and J. H. Maiden, F.C.S., F.L.S., Curator, Technological Museum, Sydney, and Superintendent of Technical Education, N.S.W., Secretaries.

Geography. — H. S. W. Crummer, Secretary of the Royal Geographical Society of Australasia (N.S.W. Branch), Secretary.

Ethnology and Anthropology.—A. W. Howitt, F.G.S., Secretary for Mines, Vict., President; John Fraser, B.A., LL.D., Sydney, Secretary.

Economic Science and Agriculture. — R. M. Johnston, F.L.S., Government Statistician, Tasmania, President; Walter Scott, M.A., Professor of Greek, Sydney University, and F. B. Guthrie, F.C.S., Consulting Chemist to the Department of Agriculture, N.S.W., Secretaries.

Engineering and Architecture.—H. C. Stanley, M.I.C.E., Chief Engineer, Southern and Western Railway Lines, Queensland, President; J. W. Grimshaw, M. Inst. C.E., M.I. Mech. E., &c., Supervising Engineer, Harbours and Rivers Department, N.S.W., Secretary.

Sanitary Science and Hygiene.—Hon. Allan Campbell, M.L.C., L.R.C.O., South Australia, President; J. Ashburton Thompson, M.D., Chief Medical Inspector, Board of Health, N.S.W., Secretary.

Mental Science and Education. — John Shirley, B.Sc., District Inspector of Schools, Brisbane, Queensland, President; Francis Anderson, M.A., Professor of Logic and Mental Philosophy, Sydney University, Secretary.

Communications and Papers for the Meeting, or inquiries, may be addressed to the Permanent Hon. Secretary, The Chemical Laboratory, The University, Sydney, N.S.W.

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Applications should be endorsed "Chemical Department."

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THE CHEMICAL NEWS.

Vol. LXXII., No. 1864.

NOTE ON THE
HEXYLENE, $C_{12}H_{12}$, AND HEXYL-HYDRIDE, $C_{12}H_{14}$, DERIVED FROM MANNITE BY REDUCTION WITH HYDRIODIC ACID.*

By J. ALFRED WANKLYN.

To-day is published, in the *Philosophical Magazine*, by Cooper and myself, an investigation of American petroleum parallel with our investigation of Russian kerosene. The hydrocarbons existing in American petroleum are members of the marsh-gas family, as was shown by the classical researches of Cahours and Pelouze, dating back to the years 1862 and 1863.

We now show that these marsh gases rise by increments of 7, and not 14 as has hitherto been maintained. Our investigation is at present confined to the more volatile part of the American oil, and we exhibit seven consecutive terms.

Having in our hands the corresponding terms of the Russian and American series, we are in a position to make a comparison of the physical characters of the two sets of liquids.

One of the most obvious facts brought out by this comparison is, that the Russian hydrocarbon is always a little heavier than the American with the same carbon-condensation. The increment of density is about 0·025 to 0·035.

More than thirty years ago, when I was working with Erlenmeyer, it fell to my lot to investigate the two hydrocarbons, hexylene and hexyl.hydride derived from mannite. Our account of these substances is published in the *Journal of the Chemical Society* for the year 1863, in our conjoint paper entitled "On the Hexyl Group."

It happens that by accident (although the sp. gr. of hexylene was determined with great care, in a thoroughly satisfactory manner) it was never published. I now place it on record.

The specimen of hexylene was prepared in the laboratory of the University of Edinburgh, by decomposing the iodide of hexyl (from mannite) by alcoholic solution of potash. The purity of the hexylene was shown by very satisfactory combustions of the substance; and here the remark may be made that good combustions afford decisive evidence of purity in a case of this kind, where no question of the presence of neighbouring homologues can arise.

Two determinations of sp. gr. at 4·8° C. and 45·5° C. were made thus:—

Sp. gr. at 4·8° = 0·6972
" 45·5° = 0·6604,

water at 4° C. being taken as unity, and the expansion of the glass being allowed for.

The sp. gr. of hexyl-hydride is given in our paper published in 1863, as 0·6645 at 16·5° C.

In the year 1864 I prepared the substance again, and made another determination of the sp. gr. at 0° C., and found it to be 0·6759; and, taking into account the circumstance that the temperature is lower than that in the former experiment, it is corroborative of the former.

By a simple calculation we are able to compare the sp. gr. of hexylene at 0° with that of hexyl-hydride at the same temperature:—

Sp. gr. of hexylene, $C_{12}H_{12}$, at 0° .. .. =0·7017
" of hexyl-hydride, $C_{12}H_{14}$, at 0° .. =0·6759

Difference .. .. =0·0258

It would thus appear that—whether the hydrocarbons are extracted by fractional distillation from a complex mixture of homologues, such as petroleum, or whether they are obtained by such a process as reduction of polyatomic alcohols with hydriodic acid—the relation between the sp. gr. of C_nH_n and the sp. gr. of C_nH_{n+2} is the same.

August 1, 1895.

CONCERNING FUMING SULPHURIC ACID.

By R. W. HILL.

The so-called Nordhausen or fuming sulphuric acid, $H_2S_2O_7$, is a compound of a molecule of ordinary sulphuric acid, H_2SO_4, with a molecule of sulphuric anhydride or sulphur trioxide, SO_3. By heating the fuming acid, the molecule of SO_3 is readily driven off.

Nearly every text-book on chemistry informs the student that this acid is still manufactured in Nordhausen, in Saxony, Germany. As a matter of fact, it was never manufactured in the said town, but in Goslar, a couple of miles from Nordhausen. At the present time, however, this acid is not manufactured at all either in or near that place; but this particular chemical branch is, practically speaking, monopolised by the large chemical concern of Johann D. Starck und Söhne, near Prag, Bohemia. They produce it in the old-fashioned manner by distilling green vitriol or ferrous sulphate,—

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

The anhydride thus given off is absorbed by rain-water or sulphuric acid, 66° Beaumé, thus producing fuming acid.

About twenty-five years ago Professor Cl. Winkler, of Freiberg, suggested the use of platinised asbestos as a "catalytic" substance for the union of pyrite—or brimstone—kiln gas, SO_2 (sulphur dioxide), with the oxygen of air. The most favourable proportions are 29·6 vol. SO_2+70·4 vol. atmospheric air (containing 14·8 vol. oxygen); but for practical purposes it is advisable to employ a dry gaseous mixture of 25 per cent SO_2+75 per cent air; the dry anhydride does not attack cast- or tinned-iron. In some works in Russia and Germany this process is actually carried out on a commercial scale, with some modifications and improvements in the old idea.

In Kalk, near Cologne, Germany, Wolter's process is used, by distilling hydric sodic sulphate,—

$$2NaHSO_4 = Na_2SO_4 + SO_3 + H_2O.$$

The sulphate of soda is then treated with sulphuric acid, in order to get again hydric sulphate,—

$$Na_2SO_4 + H_2SO_4 = 2NaHSO_4.$$

About five years ago a German chemist produced the fuming acid from the ordinary sulphuric acid by means of an electric current. Carbon plates, about ⅛th inch apart, were immersed into sulphuric monohydrate, and an electric current passed through the fluid. The water of the acid is decomposed into hydrogen and oxygen, and the SO_3 is absorbed by the electrolyte, this forming fuming sulphuric acid, $SO_3 + H_2SO_4 = H_2S_2O_7$. As soon as a layer of sulphur is observed on the electrodes, the current is reversed. As far as the writer knows, this electrical process has never been tried on a commercial scale.

Manchester, August 3, 1895.

German Association.—Dr. H. Krüss will read a paper on a "New Procedure in Quantitative Spectral Analysis" at the forthcoming Congress of the German Association of Naturalists and Physicians. At the same Congress Prof. W. Ostwald will read a paper on the "Vanquishing of Scientific Materialism"; and Prof. Svante Arrhenius will explain the fluctuations of climate in Geologic Epochs by simultaneous modifications in the proportions of Carbonic Acid in the Air.—*Chemiker Zeitung.*

---

* In this paper the atomic weight of carbon is written as 6.

GOLD AND SILVER IN COPPER AND IN COPPER MATTE.

By ERNEST A. SMITH, Assoc. R.S.M., F.C.S.

In a very interesting paper* "On a Uniform Method of Assay of Copper and of Copper Materials for Gold and for Silver," by Dr. Albert R. Ledoux, of New York City, the author referred to the discrepancies which often occur in the results obtained by different assayers working on the same sample, and suggested that some uniform method for assaying these materials should be arrived at, somewhat similar to the movement initiated by Prof. J. W. Langley, of Pittsburg, in 1888, which resulted in the general adoption of standard methods in the determination of carbon and other important elements in iron and steel. He proposed that a number of samples of gold- and silver-bearing copper material should be distributed to as many assayers as were willing to take part in the movement. In response to Dr. Ledoux's paper, a large number of establishments and assayers expressed their willingness to co-operate in the plan he proposed. The necessary samples were prepared by Dr. Ledoux, and distributed to the various parties co-operating. The results obtained have been received recently and tabulated, in a paper presented at the Florida meeting of the American Institute of Mining Engineers, and should be of interest to all those who have to assay similar materials in England. In discussing the various methods of assay in his paper, Dr. Ledoux draws attention to the fact that there is a divergence in the methods usually employed in the East and West for the assay of these copper materials. He points out that some of the Eastern public assayers use the "wet" method, which consists in treating one assay-ton (about 30 grms. or 500 grains) of the sample of copper borings or matte in a (No. 5) beaker with a mixture of 100 c.c. water and 50 c.c. nitric acid of sp. gr. 1·42. When the violent action has ceased, 50 c.c. more of nitric acid is added, and the solution heated until everything soluble is dissolved. It is then boiled until the free nitric acid is expelled; then diluted with 400 c.c. water and 5 c.c. sulphuric acid, and 10 c.c. of a concentrated solution of acetate or nitrate of lead added. The precipitate of lead sulphate is allowed to settle, filtered, and washed, and the filter and its contents are partially dried, then wrapped in thin lead-foil, and transferred to a scorifier. Cupellation is conducted in the usual manner.

This method is intended for the determination of gold, but enough silver may be present to allow the bead to be parted.

For silver the usual method in the East is to dissolve the sample in dilute nitric acid, as described above, and, before adding the lead salt, enough chloride of sodium is added to precipitate all the silver. The rest of the process is conducted as for gold.

In the West, the "all-fire" method of assay is employed almost exclusively.

At one works, ten portions of the samples, each of one-tenth assay-ton (about 2½ grms. or 50 grains), are scorified with 50 grms. of test-lead and a cover of 1 grm. of borax. The lead buttons obtained are cupelled separately, but the ten beads of precious metals obtained are weighed together. The cupels are then ground up and fused in five lots, of two cupels to each lot, with—

Litharge..	90	grms.
Boron glass	50	,,
Soda carbonate ..	50	,,
Argol	3	,,

The silver obtained, after cupellation of the resulting lead buttons, is added to that from the first assay. All the beads are then parted for gold.

Dr. Ledoux remarks that each of these methods in the hands of assayers skilled in its application will produce fairly uniform results, yet any assayer running the two methods side by side will get divergent figures for gold. It is stated that the results obtained by this method are usually higher than those obtained by the "wet" method. For mattes the same method is employed, but sometimes a second scorification is necessary, which is usually performed in a 2½-in. scorifier, with the addition of lead to make up the total to 35 grms.

The necessary samples distributed to the various assayers were prepared in the following manner:—

Copper Matte.—A carload of matte was put through a Blake crusher, then automatically sub-divided into tenths by a "Taylor and Brunton" sampler, and one-tenth passed through Cornish rolls, and then through a 12-mesh screen. This was again sub-divided by an automatic sampler into tenths, and a final tenth, representing 1 per cent of the original lot, was finished by hand sampling on an iron floor until 100 lbs. remained. This was pulverised to pass a 40-mesh screen, and then thoroughly mixed and divided, in the presence of an assistant, for distribution to all those co-operating.

Copper Borings.—These were taken from a lot of anodes, the dip samples from several batches having been united, re-melted, and cast into a plate, which was proved by assay to be of uniform quality in its different parts. Borings from this plate were intimately mixed and divided in the presence of an assistant.

The samples were stated to have approximately the following compositions:—

Copper Matte.

Copper	50 to 60 per cent.
Gold	2 to 3 ozs. per ton.
Silver	100 to 150 ,, ,,

Copper Borings.

Copper	—
Gold	0·20 to 0·50 ozs. per ton.
Silver	140 to 180 ,, ,,

The detailed methods employed in each case are given in the paper presented to the Institute at the Florida meeting, and are substantially the same as those described. The results returned by the various assayers are as follows:—

Returns for Sample of Copper Matte.

	Silver. Ozs. per ton.		Gold. Ozs. per ton.		Copper. Per cent.		
	Direct scorification.	Combined wet and scorification.	Direct scorification.	Combined wet and scorification.	Electro-deposition method.	Cyanide method.	Iodide method.
1.	127·00	130·68	2·22	2·310	55·08	54·80	55·00
2.	135·38	127·60	2·35	2·240	55·17	53·70	
3.	129·99	125·20	2·33	1·850	54·96	52·72	
4.	131·89	129·72	2·41	2·260	55·04	50·55	
5.	128·95	123·03	2·09	2·325	54·50	54·37	
6.	127·60	125·31	2·22	2·215	54·86	50·75	
7.	128·75	128·06	2·27	2·240	54·60		
8.	122·88	128·27	2·28	2·260	55·08		
9.	131·22	125·95	2·29	2·050			
10.	126·80	128·70	2·26	2·160			
11.	127·44		2·36	2·270			
12.	127·02		2·27				
13.	128·70		2·33				
14.	130·42						
Means	128·86	127·25	2·28	2·198	54·91	52·81	55·00

One "crucible" assay gave:—

123·60 ozs. of silver per ton.
2·26 ,, gold ,,

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* Read before the Bridgeport Meeting of the American Institute of Mining Engineers, October, 1894.

One combined "wet and crucible" assay gave:—

126·20 ozs. of silver per ton.
2·09 " gold "

Returns for Sample of Copper Borings.

	Silver. Ozs. per ton.		Gold. Ozs. per ton.		Copper. Per cent.	
	Direct scorification.	Combined wet and scorification.	Direct scorification.	Combined wet and scorification.	Electro-deposition method.	Cyanide method.
1.	159·33	155·34	0·30	0·29	97·45	97·98
2.	159 68	160·78	0·32	0·24	97·04	
3.	164·35	156·31	0·35	0·22	98·19	
4.	159·12	148·50	0·40	0·205	98·46	
5.	147·40	157·30	0·35	0·21	97·50	
6.	155·75	156·92	0·35	0·28	97·37	
7.	164·05	157·04	0·30	0·24		
8.	154·40	153·65	0·40	0·317		
9.	156·90	161·40	0·37	0·30		
10.	160·63	156·10		0·25		
11.		156·97		0·22		
12.		159·67		0·22		
13.		156·72		0·501		
14.		159·27		0·40		
15.		148·78		0·26		
16.		159·00		0·28		
Means	158·16	156·49	0·35	0·277	97·66	97·98

One combined "wet and crucible" assay gave:—

161·35 ozs. of silver per ton.
0·42 " gold "

From the above tables the differences between the highest and lowest results returned are as follows:—

For Copper Matte.

	Direct scorification.	Combined wet and scorification.
Silver, ozs. per ton	12·50	7·65
Gold " "	0·320=6·4 dwts.	0·475=9·5 dwts.

For Copper Borings.

Silver, ozs. per ton	16·95	12·90
Gold " "	0·100=2·0 dwts.	0·296=5 92 dwts.

As Dr. C. B. Dudley remarks (in a paper read before the Chemical Section of the Engineers' Society of Western Pennsylvania, 1892):—"There are four main causes of error to which may be attributed the discrepancies in analysis between the results of different workers:—

1. The sample may not be uniform in composition, although supposed to be so.
2. The degree of purity of the chemical reagents always varies.
3. There is a "personal error" in manipulation, and there are various causes which prevent any particular method from being carried out in the usual way.
4. The results given by each method may be regularly higher or lower than the truth."

The first cause of error is one which frequently occurs in commercial samples, and would lead to the suggestion that more uniform methods of sampling be adopted for the various materials under treatment, although in the copper materials under discussion the discrepancies are probably due in a very minor degree to errors of sampling, and much more probably due in most cases to careless work and the use of inaccurate methods of analysis and assays. For assays in which assay lead is employed it is a matter of importance to take into account the amount of silver present, and to test every fresh sample of lead received for silver, as test-lead supplied as being "free from silver" can never be relied upon. Gold is invariably present (see experiments by Richard Smith, *Phil. Mag.*, Feb., 1854) in lead, but generally in such minute quantities that it may be disregarded. The question of the silver in the lead used for the assay is often disregarded by assayers—a fact which may account for some of the discrepancies in the quantity of silver present in the copper materials operated upon.

Other, and perhaps more important sources of error, are the temperature at which the cupellations are conducted and the subsequent treatment of the buttons in the "parting" operation. Many assayers treat the buttons in one acid only in the "parting" process, and in some cases do not hesitate to use strong acid instead of dilute. The discrepancies may also be due to the want of a sufficiently accurate balance, a piece of chemical apparatus which is not always kept in the most perfect condition at metallurgical works. The errors likely to occur from this source cannot be too strongly impressed, when we bear in mind the comparatively small quantity of material operated upon, and the large increase in the error when the results are calculated to represent a ton of material.

Mr. J. W. Westmoreland, an assayer with considerable experience in the assay of copper materials, in referring to the assay of gold in bar copper (*Journ. Soc. Chem. Ind.*, Feb. 27, 1886), remarks that "the general tendency is for the gold produce to be low, sometimes to a serious degree. . . . I believe this is due to some extent to the insufficient weight of material operated upon." In using ½ oz. (240 grains) of copper chips for assay an error of 0·001 grain in the weight of the gold would amount to 3 dwts. of gold per ton (of 2240 lbs.) of copper. In the case of 1 oz. (480 grains) of copper chips, 0·001 grain would represent 1½ dwts. per ton, but by careful weighing this could be reduced one-half, or to 18 grains per ton. He also remarks that "one assayer made his gold assay on 100 grains of copper chips. In this case 0·001 grain in the weight of the gold, representing 6·5 dwts. per ton; and it must be remembered that the value of this gold varies from 2/- to 3/6 per dwt.; hence the necessity for careful and accurate work."

The results collected by Dr. Ledoux are extremely interesting, and should be of value to all those engaged in assaying copper materials for silver and for gold.

Royal School of Mines, London.

NOTE ON THE PURIFICATION OF GLUCINUM SALTS.*

By EDWARD HART,

Twenty years ago I found glucinum in a clay brought to Dr. Drown's private laboratory, in Philadelphia, for analysis. The experience gained then in making the separation from alumina showed clearly that none of the methods then known gave a satisfactory separation. In dissolving the carbonate we found that alumina also dissolves, and that in treating the oxides with solution of ammonium chloride, alumina as well as glucina dissolves.

In beginning the purification of glucina from beryl, which I have undertaken for a more careful study of the metal and its alloys, I determined, if possible, to prepare it in some other way than by the use of the time-honoured ammonium carbonate method, which, besides giving a material of doubtful purity, is expensive and tedious. Such a method has been found based on the properties of the mixed sulphates from beryl, and which seems not to have been used for this purpose. Perhaps it will be best to describe the method now used in full, without describing the failures through which the work passed.

The powdered beryl is first fused with mixed carbonates, and then ground and washed with water. The powdered mass is then mixed with sulphuric acid and

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* Read at the Boston Meeting of the American Chemical Society, December 28, 1894.

evaporated to make the silica insoluble. The sulphate solution obtained from this material is evaporated and treated with an excess of potassium sulphate. Alum crystallises out, and is purified by re-crystallisation. The mother-liquor contains the glucinum along with the iron and alkaline sulphates. Potassium chlorate is added in excess, and the solution heated to peroxidise the iron. Sodium carbonate solution is now added, little by little, the solution being boiled after each addition until a filtered sample shows no yellow colour. The whole solution is then filtered, and the glucinum which will be contained in the filtrate is precipitated by further addition of sodium carbonate.

The method, of course, depends upon the fact that it is impossible to throw down the glucinum until the greater part of the acid has been saturated, the glucinum remaining in solution as basic sulphate. Iron and aluminum, on the contrary, are easily separated. Some care is needed in order to get rid of the last trace of iron, which persistently remains in solution until the point at which the precipitation of glucinum begins is almost reached.

A sample prepared in this way was perfectly soluble in hydrochloric acid, gave no reaction for iron with potassium ferrocyanide, was completely soluble in an excess of ammonium carbonate and caustic potash. The ammonium carbonate solution gave no precipitate on the addition of ammonium oxalate. The method is exceedingly simple, convenient, and cheap, and leaves nothing to be desired. —*Journal of the American Chemical Society*, xvii., 604.

ON THE

FLUORESCENT SPECTRUM OF ARGON DESCRIBED BY PROFESSOR BERTHELOT.

Berthelot has submitted a specimen of argon sent him by Professor Ramsay to the action of the effluve. In the spectrum of the fluorescent light Berthelot was able to distinguish four lines, the wave-lengths of which, as measured with a spectroscope of low dispersive power, were as follows:—

579	millionths	m.m.
547	,,	—
438	,,	—
436	,,	—

The limit of error was given as 3 to 5 of the last figures.

The line 579 made the impression of a double line, as also 547. Besides there were also bands in the green and the violet, and especially in the red and the orange, the feeble illumination of which did not admit of a determination of the wave-length.

Berthelot ascribes the observed lines to argon, and thinks that he can recognise the following lines indicated by Crookes; the degree of brightness of which is shown by the number in a bracket, where (10) expresses the greatest brightness.

574·06	(6)
555·70	(10)
549·65	(8)
433·35	(9)
430·05	(9)

It is, in the first place, highly improbable that among the numerous bright lines of the argon spectrum only *these* should be left under the action of the effluve. Why, *e.g.*, did not the lines—

603·8	(8)
565·1	(9)
561·0	(9)
518·58	(10)

make their appearance?

The interpretation of Berthelot's observations is probably this: That he has observed the *spectrum of mercury*, and probably traces of the nitrogen spectrum.

The brightest lines of the mercurial spectrum, according to Thalén are—

578·96	(10)
576·81	(10)
546·06	(10)
435·81	(10)

and agree with Berthelot's value as closely as might be at all expected. Thalén's first two lines correspond to line 579, seen double by Berthelot. We should ascribe Berthelot's line 438 to mercury, and 436 to nitrogen, which has a bright band at 734·60.

We have further satisfied ourselves, by our own observations, that at high pressures a small addition of nitrogen to argon suffices to suppress almost entirely the argon spectrum.

The bands observed by Berthelot in the red, yellow, green, and violet have probably belonged to nitrogen.

We have repeatedly prepared argon, and in some cases we have also obtained a mercuriferous gas which showed Thalén's four above-mentioned lines in full lustre. The conditions under which the metallic mercury used in the apparatus is taken up by the gas we are not yet able to give, but acetylene seems here to play a part which in Berthelot's experiments may have been formed from the accompanying benzene vapour by the action of the effluve.—*Liebig's Annalen*, cclxxxvii., p. 230.

QUANTITATIVE ANALYSIS OF GALENA.

By P. JANNASCH and H. KAMMERER.

One of the present writers has formerly proposed several methods for the analysis of galena. The precipitation of the alkaline (sodium) solution of the sulphide oxidised to sulphate by the direct addition of bromine, and also the precipitation by hydrogen peroxide of an ammoniacal solution in ammonium acetate, were recommended as especially simple; and, finally, as the most expeditious, the decomposition of the mineral in a current of bromine. The precipitation of the lead in an alkaline solution (potassic) by means of bromine was subsequently also used by L. Medicus, the halogen being applied in the form of vapour.

0·7 to 0·75 grm. of finely pulverised galena is placed in a porcelain capsule and moistened with dilute nitric acid, allowed to stand in the cold for some minutes, treated there with 10 c.c. of concentrated nitric acid, heated on the water-bath, and suitably evaporated. Nitric acid and water are added afresh, along with 10—15 drops of bromine, and heated, with frequent stirring, until all the sulphur is completely oxidised to sulphuric acid.

For the certain destruction of any bromate formed as a subsidiary product, we evaporate the saline mass three times with concentrated nitric acid until dry as dust. When this has been effected, the dry residue is boiled for a short time in a covered capsule with 60 c.c. of water and 20 c.c. of concentrated hydrochloric acid, so as to dissolve all the lead sulphate. The residual gangue is filtered off (using a tall beaker), the filter and the tube of the funnel are well washed with boiling water, incinerated, and weighed.

For precipitating the lead, the filtrate is heated to ebullition on a free flame until complete solution has been effected, and the liquid is poured into a previously prepared mixture of 25 c.c. water, 50 c.c. hydrogen peroxide, and 50 c.c. concentrated ammonia. The lead is thus precipitated as a fine yellowish red partially crystalline deposit, the composition of which will be determined subsequently. The whole is allowed to stand covered for several hours, with occasional stirring, filtered, washed carefully with cold water, dried, and weighed in a platinum crucible as lead oxide.

For the determination of the sulphuric acid, the filtrate from the lead precipitate is evaporated on the water-bath until the odour of ammonia has disappeared; 5 c.c. of concentrated hydrochloric acid, and the same volume of alcohol are added, and the whole is gently heated for some time in order to re-generate certain quantities of persulphuric acid and to destroy with certainty any hydrogen peroxide still present. The sulphuric acid is then precipitated with the calculated quantity of solution of barium chloride. If this precaution is omitted, the results are much too low, in consequence of the solubility of barium persulphate.

Small impurities of a galena, consisting of copper, nickel, zinc, or arsenic, will be found in case of the hydrogen peroxide method in the ammoniacal filtrate, and after the separation of the sulphuric acid may be separately determined by barium chloride.—*Berichte*, 1895, No. 11, p. 1409.

ON THE RECOGNITION OF BLOOD SPOTS IN JUDICIAL CASES.

By FRIED. GANTTER.

The detection and demonstration of traces of blood upon rusty iron is known to be hindered, and in many cases rendered impossible, by the circumstance that it is not practicable to obtain crystals of hæmine, or to effect other reactions for the demonstration of blood from the substance which has been rendered insoluble by the ferric oxide. As a rule, in such cases, the result of the investigation—especially if it has had to be undertaken after prolonged contact with the rusty iron—is to this effect, that it has not been possible to show the presence of blood with certainty; but that this, in view of the great difficulty of recognising blood under such conditions, is *no* proof of the total absence of blood upon the article in question. But very often it is not merely to show the *presence* of blood, but quite as important to give a certain proof of its entire *absence*, *i. e.*, to prove that the spots in question are certainly *not* due to blood.

For the latter purpose the behaviour of the blood-substance with hydrogen peroxide is a good means. If a drop of the solution of hydrogen peroxide is brought in contact with the slightest trace of the substance of blood, there occurs immediately a distinctly visible evolution of oxygen gas proceeding from the blood, and gradually increasing, so that the drop is very soon converted into a white frothy mass, which retains its froth-like character for a long time. This reaction is most distinctly manifested as follows:—

Upon a port-object — which for the sake of greater distinctness we lay upon black paper—we place a drop of the solution of the blood substance, or, if such a solution cannot be obtained, as in case of spots on rusty iron, a small portion of the scrapings of the rust, which is covered with a drop of a very weak alkaline water, and allowed to stand for some minutes to soften the blood substance. We then add a drop of solution of hydrogen peroxide, when, if the smallest trace of blood substance is present, relatively large gas-bubbles are evolved; in case of sanguiferous rust, we see that the development of gas does not proceed uniformly from all parts of the rust, but merely from certain points, *i.e.*, from such only to which particles of blood adhere. The gas-bubbles, after some time, coalesce to a tender froth, which on the black paper appears snow-white, and which remains for some hours without melting away. It is a characteristic feature that this froth contracts from the margin of the drop towards the middle, so that the sharply limited white foam appears surrounded by a ring of clear liquid,

To mistake the phenomenon for ordinary air-vesicles is scarcely possible. Certainly, on moistening the rust with the feebly alkaline water, single air-bubbles often appear, but they soon disappear if touched with a slender glass rod before the hydrogen peroxide is added.

If the reaction does not appear it is certain evidence that the rust-spots contain no blood. Inversely, however, the appearance of the reaction is no positive evidence of the presence of blood, since the animal fluids, *e.g.*, pus, behave with hydrogen peroxide in the same manner as blood.

The reaction may also be usefully applied for the closer examination of the crystals of hæmine, if, as it sometimes happens, we are in doubt whether the crystals obtained are really those of hæmine. If we treat the microscopic preparation containing the crystals in the manner described above, there occurs at once a strong development of gas, whilst no change occurs if the crystals are other than those of hæmine.

The reaction is also suitable for a convenient preliminary examination of spots supposed to be blood. The age of the spots upon rusty iron does not seem to have any marked influence on the distinctness of the reaction; at least spots six months old showed the reaction as sharply as those freshly obtained.—*Zeit fur Anal. Chem.*, vol. xxxiv., p. 159.

QUANTITATIVE DETERMINATION OF HYDRAZIN IN ITS SALTS.

By JULIUS PETERSON.

For this purpose Peterson utilises its well-known reductive action with Fehling's solution or with potassium permanganate.

Curtius (*Journ. Prakt. Chemie*, N. S., xxxviii., p. 418) recommends boiling the hydrochlorate with hydrochloric solutions of platinum chloride, and collecting the nitrogen evolved. The process takes place according to the equation—

$$N_2H_4,2HCl + 2PtCl_4 = N_2+6HCl + 2PtCl_2.$$

The author's experiments show that the proportion of nitrogen obtained is too high by about 1 per cent.

The volumetric method depends on the use of iodine, and is founded on the following reaction:—

$$5N_2H_4H_2O + 4I = 4(N_2H_4,HI) + 5H_2O + N_2.$$

It is applicable only for the hydrate, and is therefore of no universal importance.

Peterson's attempts to determine hydrazin with boiling Fehling's solution show that the process takes place according to the equation—

$$N_2H_4 + O_2 = 2H_2O + N_2.$$

The author was not able to obtain constant results by titration; but a perfectly accurate determination of hydrazin can be effected by collecting and measuring the nitrogen liberated.

Peterson proceeds in the same manner as Strache in his determinations of the carbonyl-number.

The determination is effected as follows:—

In a small flask, holding about 25 c.c., and capable of being closed with a caoutchouc stopper having two perforations, there is introduced a quantity of Fehling's solution, excessive in proportion to the substance to be used, and previously diluted with water to about 60 c.c., and heated to boiling. The stopper of the flask contains, in one of its perforations, a small glass tube, introduced from below, containing the weighed substance, and a small glass rod introduced from above. In the other perforation is a gas-delivery tube, through which the air is first expelled by watery vapour. When this has been effected, a measuring tube (filled with water previously boiled out) is placed over the gas-delivery tube, the lamp beneath the flask is withdrawn for a moment, and the little tube containing the substance is thrown into the liquid by pushing in the glass rod. After a brief ebullition all the nitrogen is driven over, and can be measured in the usual manner. The tube used for introducing the substance contains about $\frac{3}{10}$ c.c. As it cannot be entirely filled, a correction of about $\frac{1}{10}$ c.c. is made in the volume of the nitrogen.

Hydrazin may also be determined by titration with potassium permanganate in a hot solution.

The titrations must be effected at 60° to 70°, and the solution must contain from 6 to 12 per cent sulphuric acid. We titrate in the ordinary manner. The titration is completed when, on further addition of the solution of permanganate, the liquid becomes more and more deeply coloured, when we titrate back with oxalic acid.

The oxidation, according to the author's experiments, takes place according to the equation—

$$17(N_2H_4,H_2SO_4) + 13O = \\ = 13H_2O + 7(NH_4)_2SO_4 + 10N_2 + 10H_2SO_4.$$

The accuracy of the equation is proved by the consumption of the permanganate, the determination of the ammonia formed, as well as by measuring the nitrogen liberated.—*Zeit. Anorg. Chemie*, vol. v., p. 1.

ACTION OF THE INFRA-RED RAYS UPON SILVER SULPHIDE.

By H. RIGOLLOT.

It is known that silver sulphide, sensitive both to luminous and obscure radiations, may be employed as an electro-chemical actinometer. I have studied the action of the infra-red rays upon this compound, and have examined if the sensitiveness of silver sulphide to radiations is a thermo-electric action or depends on some other cause.

Two plates of silver sulphide, immersed in a dilute saline solution, formed an electro-chemical actinometer. The sulphuretted plates were prepared by electrolysing a solution of sodium sulphide by a feeble current for two minutes. They were about 2 m.m. in width by 40 m.m. in length; they were paraffined on the sides facing each other, one only being exposed to the radiations studied. The actinometer, connected either to a Thomson galvanometer of the resistance of 25,000 ohms, or to a Lippmann electrometer, was successively exposed to the various radiations of a prismatic spectrum of the length of 55 m.m. from the rays D to G.

Under these conditions the sensitiveness of silver sulphide for the infra-red radiations is recognised to a great distance from the last visible radiations. The galvanometer still gives indications for the wave-length μ 1·32, and we find in the solar spectra the two minima at μ 0·96 and μ 1·16, and the chief maximum μ 1·04 as signalised by Langley. The electromotive force developed by the most active part of the infra-red spectrum, the slit having only the width of 1·4 m.m., is of 3 to 4 thousandths volt. In the visible spectrum the sensitiveness decreases very rapidly from the ray A to the ray F, becoming then negligible. The illuminated plate is always negative with reference to the other, whatever may be the solution employed.

In another series of experiments, in order to compare the thermo-electric effects with the luminous effects, there were employed plates of a greater breadth, about 6 m.m.; each of the two plates plunged into one branch of a U-tube of glass, containing a very dilute solution of silver nitrate or of sodium chloride. One of the limbs of the tube was surrounded with a glass jacket, and by filling the annular space with hot water we could establish between the two limbs of the U-tube a difference of temperature, ascertained by means of thermometers immersed in each limb. On the other hand, in the tube itself, the plate intended to be heated might be illuminated by a Bengel burner, the luminous intensity of which corresponds to that of a Carcel lamp, placed at the distance of 0·20 metre. The light fell upon the plate only for a very short time, the effect produced being instantaneous. The electromotive forces developed, whether by the difference of temperature or by light, were recorded as above.

It was observed that the light instantly produced a negative electromotive force of about $\frac{2}{1000}$ volt, and that, on heating, it was necessary to establish between the two plates a difference of temperature of 6° to 7°, to develope the same electromotive force, negative in silver nitrate, positive in sodium chloride.

On taking as liquids dilute solutions of NaBr, NaI, KBr, KI, K_2SO_4, $MgSO_4$, $AgSO_4$, $C_2H_3AgO_2$, it was found that the illuminated plate is always negative with relation to the other, whilst the heated plate is negative only in solutions of salts of silver, and positive in solutions of the other salts tried.

The two series of experiments are certainly not identical, but I believe that they have a sufficiency of points in common, so that there being the difference of temperature necessary to develope an electromotive force of 0·002 volt, it would be difficult to admit that the action of the infra-red rays is merely thermic.—*Bull. de la Soc. Chim.*

REPORT OF EXPERIMENTS ON THE CHEMISTRY OF THE CYANIDE PROCESS, AND NOTES ON ITS WORKING.

New Process for Determining Cyanides.

Solubility of Gold in Double Cyanides and in Hydrochloric Acid.

Phenolphthalein as an Indicator in Titrating Potassium Cyanide.*

By G. A. GOYDER, F.C.S.,
Analyst and Assayer to the South Australian School of Mines and Industries.

When at the Government cyanide works at Mount Torrens in April last I noticed that the process in general use for determining the amount of "available" or simple cyanide of potassium, namely, titration of a known volume of solution by means of a standard solution of nitrate of silver, with the addition of a little potassium iodide to give a sharper end reaction, although it gave accurate results with ordinary solutions of potassium cyanide, in the presence of double cyanide salts the end reaction was ill-defined, and after making numerous experiments it appeared that in titrating the sump solutions, which contain much of their cyanogen as the double cyanide of zinc and potassium, the end reaction was not only ill-defined, but that the quantity of nitrate of silver required to produce a permanent turbidity increased with the dilution, with the temperature, and also with the amount of simple cyanide added to a greater extent than was calculated. Thus a sump solution, which titrated cold indicated 0·015 per cent of simple cyanide of potassium, after heating quickly on a water-bath indicated 0·07 per cent, or nearly five times as much. If, however, the heating and titration are done slowly much of the cyanogen is decomposed and lower figures obtained. A cold sump solution, to which nitrate of silver has been added to permanent turbidity on shaking, always clears on being heated. A 1 per cent solution of crystallised double cyanide of zinc and potassium on titration as above appeared to contain one-thirtieth of its total cyanogen as simple cyanide of potassium; on diluting to sixteen times the bulk it indicated one-third of the total as simple cyanide, and by further diluting to two hundred and fifty times the bulk the whole of the cyanogen appeared by titration to be simple cyanide.

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* From the Sixth Annual Report of the Council, Adelaide 1895.

As regards the indefiniteness of the reaction, a sample of sump solution was divided into three equal portions. To No. 2 an equal volume and to No. 3 two volumes of distilled water were added, and these were given to an expert, well acquainted with the process, but not knowing how the solutions were made up, to test. He reported that No. 1 contained 0·04 per cent, No. 2 0·05 per cent, and No. 3 0·04 per cent of simple cyanide. It is evident that if No. 1 contained 0·04, No. 2 could only have contained half, and No. 3 one-third of that amount if the process were reliable.

Again, a sample of sump solution, which by the above test contained 0·02 per cent of simple cyanide, was strengthened up by pure cyanide of potassium, so that it was calculated to contain 0·09 per cent, but it now appeared to contain 0·15 per cent, so that at least 0·06 per cent of double cyanide was returned as simple cyanide. There may, however, be cases in which the addition of cyanide of potassium to sump liquors would not have this effect. Thus, supposing the solution to contain the double cyanide of iron and potassium, the addition of the proper amount of cyanide of potassium to this would produce ferrocyanide of potassium, $K_2FeCy_4+2KCy=K_4FeCy_6$, and on titration the cyanide of potassium would be found to have disappeared. In actual work, therefore, the results obtained by this method are only comparative, and it would indicate to some extent where a large excess of cyanide was used in lixiviation. If the solutions were alkaline the indications would again be interfered with, as will be shown by what follows.

I therefore modified the above process by adding a decided excess of caustic soda to the sump solutions before testing. If a precipitate is produced it is better to add, say, 10 c.c. of 5 per cent caustic soda to 20 c.c. of sump solution, shake, pass through a dry filter, and take 15 c.c. of the filtrate for titration. When this solution is titrated with nitrate of silver after the addition of a little potassium iodide the end reaction is exceedingly sharp; a decided excess of caustic alkali does not interfere, and the precipitate is not dissolved by heating. This method, however, not only indicates the simple alkaline cyanide present, but also the cyanogen present in the original solution as zinc-potassium cyanide. This process was used by me at Mount Torrens last April in watching the progress of lixiviation, and its indications gave much more exact information as to the progress than could be obtained by the ordinary process. According to an extract from the *Journal Chemical Industry*, Nov., 1894 ("The Cyanide Process"), W. R. Feldtmann (*Engineer and Mining Journal*, lviii., 1894, 218—219) has experimented with this process, and states:—"Addition of alkali to working solutions which have become somewhat weak in alkali brings up the strength by regenerating, *i.e.*, decomposing the zinc cyanide, . . . so that, as a matter of fact, when the solutions are pretty strongly alkaline they contain no zinc as cyanide, but only as hydrate dissolved in alkali (zincate of potash, &c.)."

But I believe that caustic alkali is never added in large excess to the lixiviating solutions, and when added in small quantities the double decomposition would not be complete, and its amount could only be calculated by applying the laws of chemical mass action after finding the relative proportion of the double cyanide of zinc and potassium to caustic alkali, and the velocity of combination of the resulting salts. As in practice this problem is complicated by the presence of the double salts and caustic potash as well as other salts, its solution is probably impossible. It may, however, be taken for granted that when caustic alkali is added to a solution of double cyanide of potassium and zinc in molecular proportions the resulting solution will after a little time contain zincate of potash, cyanide of potassium, and the double salt.

Having recently found that hydrocyanic acid does not decolourise phenolphthalein, and that cyanide of potassium is alkaline to that indicator, while the double cyanides are neutral, I have endeavoured to base on these reactions a new process for finding the amount of simple cyanide of potassium present in sump liquors, &c. In the presence of caustic alkali or alkaline carbonates this process could not be applied; bicarbonates do not interfere if the titration is made in a stoppered bottle with the necessary precautions. The titration is made by measuring 100 c.c. of sump solution, or solution after passing through the tailings, into a stoppered bottle, adding 1 c.c. of one-twentieth per cent phenolphthalein and running in decinormal hydrochloric acid till the pink colour is destroyed; 1 c.c. of the acid = 0·0065 per cent of cyanide of potassium present. By this reaction I have found that as a rule the sump solutions do not contain more than 0·0004 to 0·002 per cent of simple cyanide of potassium as a maximum amount, and that from this amount any caustic alkali or alkaline carbonate present must be deducted, so that it would appear that the solutions after passing the zinc boxes contain practically no simple cyanide of potassium, but that it is all converted into double salts. The following analysis of sump liquor from Mount Torrens confirms this opinion:—

Analysis of Sump Liquor from Mount Torrens after Passing Zinc Boxes.

Analysis.	Per cent.
Copper	0·0030
Zinc	0·0178
Iron	0·0061
Calcium	0·0145
Magnesium . ..	0·0042
Potassium	0·0609
Sodium	0·0645
Chlorine	0·0875
Cyanogen	0·0477
Sulphuric acid radicle	0·0401
Carbonic acid radicle	0·0333
Total.. ..	0·3796

Assumed composition of salts in solution.	Per cent.
Ferrocyanide of potassium ..	0·0400
Copper-potassium cyanide	0·0072
Zinc - potassium cyanide	0·0676
*Calcium carbonate	0·0362
*Magnesium carb.	0·0147
*Potassium carb...	0·0025
Potassium sulphate	0·0431
Sodium sulphate .	0·0241
Sodium chloride .	0·1442
Total.. ..	0·3796

* The carbonates would be in the solution as bicarbonates, but are here given as simple carbonates to facilitate comparison.

In addition to the above, the solution also contained traces of cobalt, mercury, silver, and gold. The flour mercury retained in the tailings from the battery is dissolved by the cyanide; some of it is again precipitated in the tailings by any soluble sulphide present in the solution, and the bulk of the remainder is precipitated in the zinc boxes. The quantity of mercury in the gold slimes from the zinc boxes is sometimes large in amount, and makes the fumes rising from them during ignition decidedly poisonous.

When discussing with Mr. L. W. Grayson, the manager of the Government plant at Mount Torrens, the alterations necessary to the old plant, I suggested that the 2-in. pipes leading from the bottom of the lixiviation vats, which are 8 ft. in diameter, should be reduced to ½-in., and that syphon bottles should be attached to the lower ends of these pipes by indiarubber tubing, the neck of the bottles being also furnished with indiarubber tubes, which could be directed into the openings of main lines of pipes leading respectively into the waste water tanks, the weak solution, and strong solution zinc boxes. These suggestions were carried out by Mr. Grayson, and it was found on testing them, that these small pipes, as soon as the solutions started running from the vats, became filled, and exerted a suction equal to between 4 ft. and 5 ft. of water—their vertical height—and thus hastened the rate of lixiviation, or permitted of tailings with a larger proportion of slimes being treated than would have been possible had the 2-in. pipes been retained, as the solutions could not be run through the tailings at such a rate as to fill 2-in. pipes, and unless full they could not produce any suction. The progress of lixiviation can be readily judged by the appearance of the solution passing through the syphon bottles, and the rate of flow adjusted by taps at the lower end of the pipes near the bottles. With tailings of moderate fineness these taps are only one-third to one-half open to produce the requisite rate of flow.

The method of conducting the lixiviation suggested by me as suitable for the Mount Torrens plant was as follows:—During the filling of a vat the tap of the draw-off pipe was left open, and the syphon bottle removed, so that as much water as possible was drained off from the tailings. Each truck-load was levelled down with a rake until the vat was nearly full; the top was then levelled as accurately as possible, and strong solution of about 0·2 per cent cyanide of potassium to the amount of about one-third the weight of the ore was run in at the top. This solution, if the vat had been well and evenly filled with tailings, sank slowly and almost without a bubble, driving the interstitial air before it, and out by the draw-off tap at the bottom, whence it escaped with considerable force, and displacing the residual water which, after a time, escapes by the draw-off pipe in general quite clear and colourless. As soon as the air has all escaped and the water flows in a steady stream, the syphon bottle is attached and the stream directed to the waste water tank. After a further interval, the liquid in the bottle begins to assume a yellowish tint, when the stream is directed into the small zinc boxes, and the rate of flow reduced, so that the strong solution displaced by the addition of an equal bulk of weak or sump solution at the top, would flow through in the time found by experience to afford the best payable extraction. When the last of the weak solution has sunk to the level of the top of the tailings, wash water is added to displace it, and the rate of flow may be now increased to save time. When the solution in the syphon bottles has again become nearly colourless, the lixiviation process is finished. The importance of having the draw-off pipe at the lowest point of the vat, and having the bottom of the vat sloping towards it from all directions, may be noted here. In such a case the water and different solutions have scarcely any tendency to mix, and the line between them is sharp, and therefore the bulk of the residual water first coming out can be run away without danger of loss of gold, instead of being mixed with the cyanide solution, diluting it, and increasing its bulk. At the end, too, the last of the weak solution is displaced with much less admixture of water, and as the bulk of solutions in stock is always kept about the same, the care exercised in properly constructing the vats is more than repaid by a saving of gold and of cyanide.

(To be continued.)

A NEW BACTERIAL PIGMENT.

By ALBERT THORPE.

As the chemistry of the bacterial pigments is a subject which has been very little investigated, the present note may be of interest.

I have isolated the brown pigment from infusions of maize undergoing putrefaction by means of the *Bacterium brunneum*. This pigment is soluble in alcohol, and is precipitated from an alcoholic solution by the addition of water. The precipitate, after filtration, was re-dissolved in alcohol, and the solution evaporated to dryness at 40° C. The following figures were obtained on the analysis of this pigment:—0·4764 grm. of substance gave 1·358 grm. of CO_2 and 0·232 grm. of H_2O.

	Found.	Calculated for $C_{18}H_{14}O_3$.
Carbon	77·74	77·69
Hydrogen . ..	5·62	5·03
Oxygen	—	17·28

From the foregoing percentage composition, $C_{18}H_{14}O_3$ represents the formula of this brown pigment.

The alcoholic solution of the pigment gave no characteristic absorption-bands when examined by means of the spectroscope.

This pigment is soluble in alcohol, ether, and chloroform, insoluble in water and carbon disulphide, and acids appear to destroy it.

NOTICES OF BOOKS.

Life and Labour of the People in London. Edited by Charles Booth. Vol. VI., Population Classified by Trades (continued). 8vo., pp. 383. London and New York: Macmillan and Co. 1895.

This work contains much interesting matter, but also much that cannot come under our cognisance at all.

The total number of persons employed in the manufactures of surgical, "philosophical"—we strongly object to this term—and electrical instruments is 8258, more than half of whom are engaged in the production of electrical appliances, and 2000 of whom are under 25 years of age.

As regards surgical instruments, we are not sorry to learn that the hospitals and the leading operators do not approve of importations from the Continent. Microscopes of German make are, on the contrary, highly appreciated. In this and the kindred trades a really good workman is at a premium.

Concerning the manufacture of spectroscopes, chemical balances, and other requisites for the physical and chemical laboratory, we believe that an increasing proportion are of German make. The same fact must, beyond doubt, be admitted concerning glass and porcelain scientific apparatus. In the coloured glass manufacture we find it remarked that an Italian or French working man might perhaps develope an artistic sense of his own, but this, apparently, an Englishman can rarely do. This is a fact gravely to be regretted. Concerning the pottery trade, we learn that "betting, even more than drink, is now the ruling extravagance."

The persons employed in the chemical arts amount to 5836, a portion of whom are merely manufacturers of blacking, of matches, and of "proprietary" medicines. The rank and file of the chemical workmen earn little more than 25s. per week. There is no complaint of unhealthiness, save in the white-lead works. Among the match-makers necrosis in the jaw is greatly decreasing. Still it is very desirable that the use of white phosphorus should cease entirely. Indeed the entire elimination of phosphorus in the match-trade, and that of white-lead in pigment-making, rank among the most important problems of chemical industry.

Concerning soap, we think that Mr. G. H. Duckworth goes too far in asserting without qualification that "the fats used are of the most disagreeable nature." What of the Russian and Australian tallows, the palm- and cocoa-nut oils? The total of the persons employed in this business, and in bone-boiling, candle-making, &c., amount to 2195, and their wages rarely exceed 30s. weekly.

The unsavoury businesses of the tanner, fellmonger, currier, furrier, &c., employ 15,739 persons. The men employed are accused—we fear truthfully—of a tendency to drink to excess. The employment, especially of those who prepare furs for the hatters, is unhealthy, and no type of respirator hitherto devised has been found suitable.

As for the textile trades we are, of course, most concerned with the dyeing and cleaning departments. Dyeing on the large scale, as applied to new goods, can scarcely be said to exist in London, though the garment dyer, once numerous, is gradually diminishing. Leaving out of the question provincial competition, the London garment dyer is now poached upon by the monopolist draper and by the jobbing tailor. The number of persons employed in the trade is now given as 1946. Concerning health there is little room for complaint. Indeed, in the manufacturing districts of Yorkshire and Lancashire, it is a common saying that a dead dyer is as great a rarity as a dead donkey. The chief peril to the dyer and cleaner springs from the ignition or explosion of the vapour of "benzoline spirit." Two injurious substances encountered in the waterproofing business are sulphur chloride and carbon disulphide. Hitherto no method of obviating their hurtful effects, or of superseding them by means of any harmless substance, has been elaborated.

The general impression produced by a perusal of this work is far from pleasing. We see a number of trades declining, and in many others the average remuneration obtained by the workers is not sufficient for the demands of a healthy life.

The Manufacture of Aluminium Sulphate (Die Fabrikation von Schwefelsaurer Thonerde). By Dr. Konrad W. B. Jurisch, Docent at the Royal Technical High School, of Berlin. Berlin: Fischer & Heilmann.

We have here a useful monograph of aluminium sulphate, or, as it is sometimes called, "concentrated alum." The author describes the raw materials, their sources, the process of manufacture, the properties and applications of the finished product, and the statistics of the trade.

Analyses are given of native sulphates from various parts of the world, the best being apparently that from Adelaide. The alum-shales and native alum-earths are correctly pronounced of little value for the manufacture in question.

The number of patents for the production of aluminium sulphate is truly appalling. But it is evident that the early attempts to use clays and felspar for the manufacture either of alum or of aluminium sulphate are being more and more restricted, since bauxite—a far preferable material—is now obtainable in increasing quantities. Cryolite ($6NaF,Al_2F_6$) is indeed an excellent material; but the only locality where it is obtained in quantity and in full purity is Arsak, in the south of Greenland. A sample from Miask was found not free from ferric oxide. Cryolite is at present used only at the Oeresund works, near Copenhagen, and at the Natrona works near Pittsburg, in Pennsylvania.

Eglinton clay is mentioned as a raw material, but its composition is not stated. The product contains 0·15 to 0·20 per cent Fe, and is consequently unfit for the uses of the paper-maker and the tissue-printer. We fear that some confusion in terminology has crept in, since we have heard the name Eglinton clay used as a synonym for gibbsite.

Bauxite is described as the leading material for the production of sulphate of alumina. The best quality is that from the neighbourhood of Belfast, as used by P. Spence and Spence Brothers of Manchester, and raised by the Irish Hill Mining Co. The best quality, the so-called "Gertrude-bauxite," contains only 0·53 per cent of Fe_2O_3, whilst many French sorts contain upwards of 20 per cent of this very troublesome impurity.

In working up bauxites the process generally followed is that of Lechatelier, which consists essentially in ignition with soda, lixiviation with water, filtration, and precipitation with carbonic acid, which of course throws down aluminium hydroxide; filtration and re-solution in sulphuric acid, which on cooling yields the commercial "cake-alum." For the details we must refer to the work of Dr. Jurisch. The outlook of the manufacture is very fairly summed up in the words that the present task of the cake-alum maker is to produce regularly and certainly an aluminium sulphate as free as possible from iron, containing from 14 to 14.5 per cent Al_2O_3, containing neither free acid nor excess of alumina, and giving a clear solution in water.

There is given an extended table showing the specific gravities and the percentage contents of solutions of cake-alum from 1·005 to 1·341.

The basic sulphate $Al_2(HO)_2(SO_4)_2$ is precipitated on dilution.

The impurities most dreaded in commercial cake-alum are iron and free acid. Samples containing from 0·003 to 0·01 per cent of iron are commonly said to be free from iron, though many dyers and tissue printers dread even these traces, in the case especially of pink and rose shades, and hence prefer ordinary alum. Traces of iron, not exceeding 0·05 per cent can be determined colorimetrically. The free acid in cake-alum rarely exceeds 0·5 per cent. It is allowed by the maker to remain, not on account of the difficulty of its removal, but to give the product a better colour. In presence of free acid, 0·05 per cent of ferric oxide does not occasion a yellowish colour.

The uses of cake-alum are as a mordant—or material for mordants—in dyeing and tissue-printing, in paper-making, in the sizing process, and in tawing hides (in these applications the absence of iron is most essential), and as a purifier for sewage and waste waters containing organic pollution. For this last purpose the presence of ferric sulphate—as in Spence's alumino-ferric cake—is not at all objectionable. We may remark that where hydrochloric acid is available, an aluminium hydrochlorate, obtained either from hydrargyllite or from iron slags, is preferable to the sulphate for the treatment of sewage.

Dr. Jurisch, by the publication of this work, has conferred a substantial benefit upon the producers and consumers of cake-alum.

Cape of Good Hope, Department of Agriculture. Report of the Senior Analyst on the Analytical Laboratory for the Year 1894. Cape Town: W. A. Richards and Sons. 1895.

The Analyst reports that the work of the Department has increased progressively from 47 in 1889 to 506 in 1894. The three Government Laboratories of Cape Town, that connected with the Adulteration Act, with the Department of Agriculture, and with the Geological and Irrigation Office, have been amalgamated.

The substances given in for analysis were very promiscuous, samples of milk being the most numerous. Of the 124 samples 42 were found to be adulterated, and of the 38 coffees 10 had been sophisticated. In case of milk, the fraud has consisted in skimming and in the addition of water. The milk of a cow, in an advanced stage of phthisis, showed:—Total solids, 9·39; milk fat, 2·60; solids not fat, 6·79; and water, 90·61.

The adulteration of coffee was solely with chicory, which in one case—from Kimberley—reached the alarming proportion of 67 per cent! One sample of whisky was totally factitious. The samples of pepper examined were all found to be genuine.

Of gold-quartz 54 samples were examined, of which 25 showed not a trace of gold. Of the samples received from Mashona Land two contained 1¾ ounces per ton, and one as much as 6¼ ounces.

Three samples of coal were found to be of fair quality, and an anthracite from Xalanga, in Tembuland, is likely to prove of great value.

The only sample of nitre sent in was one from Prieska, containing 78·9 per cent of potassium nitrate.

A lode of sulphur in admixture with graphite may be valuable if the finder is not mistaken as regards its extent.

The waters were not satisfactory. That from the Gamtoas River Bridge is more saline than the Indian Ocean. Out of 23 samples of water only 5 were fit for use, 7 doubtful, and the rest polluted and unfit for use. Out of 81 samples of well-water 71 were bad, including 29 from Cape Town and its district.

The soils show generally a deficiency in phosphoric acid, and in many instances also in potash.

A sample of peat-ash from Durban was found exceedingly poor.

Two native barks contained respectively 25 and 26 per cent of tannin. If abundant they may be exported to advantage.

Two samples of Cape tea have been examined. These were not ordinary teas grown in Africa, but were obtained from native shrubs. They contained no theine or any similar alkaloid.

L'Industrie Chimique (Chemical Industry). By A. Haller, Director of the Chemical Institute of the Faculty of Sciences of Nancy, Correspondent of the Academy of Sciences and the Academy of Medicine. Pp. 348. Paris, J. B. Baillière et Fils. 1895.

This compact work forms the first volume of a series entitled the "Encyclopædia of Industrial Chemistry and Metallurgy." It treats more especially of higher instruction in different countries; of the products of the heavy chemical industry, the works, and their recent improvements; of chemical and pharmaceutical products, especially the products little known or recently discovered; artificial colouring matters; essential oils, and raw materials for perfumery.

The first of these heads is of the deepest and most general interest. It is admitted that the German chemical manufacturers are constantly growing at the expense of those of France and Britain. The causes of this superiority are manifold; but first and foremost stands the organisation of the German Universities, who are here aptly pronounced to be "the makers of the national glory and prosperity." There is no restraint, no subjection to any narrow pre-arranged "syllabus." The professors enjoy that freedom of spirit which is most favourable to high culture, and which is not met with in any other country. The interference of the public authorities in questions of the *personnel* of a university is as restricted as possible. The universities, though dependent on the State and paid by it, enjoy an autonomy which enables them to choose their rectors, their deans of faculty, and their professors, and present them to the Minister of Public Instruction for formal nomination, and it is very rare for the Government to interfere with the choice of the *Senatus Academicus*.

To be called to the occupation of a chair it is not necessary to produce numerous certificates, to undergo depressing competitions which throw no light on the originative power of the candidate. It is merely requisite for him to have given proof of originality in research, and to have manifested himself a pioneer in Science. A *Rector Magnificus* — a dignitary essentially equivalent to the Chancellor of an English University or to the Lord Rector in Scotland — has not to undergo, like the latter, election on the principles of political faction, or to be selected by a body consisting mainly of half-pay officers. A candidate for a professorship of experimental science has not to be "heckled" on points of theological controversy or to sign a confession of faith. The student has not to waste precious time and priceless brain-power in preparing for successive examinations, and the inventor has not to meet the interference of alien patentees who obtain patents without any intention of practising them upon German soil. To meet with competition so arranged our industrialists, bound as they are by a vicious system, would have to be superhuman.

It is interesting to find that the institutions of higher instruction cost only 5d. annually per head of the population. Are they not an incomparably better investment than the Board Schools of Britain?

Besides the twenty-two Universities of the German Empire, the Polytechnic Schools of Aix-la-Chapelle, Carlsruhe, Brunswick, Charlottenburg, Darmstadt, Dresden, Hanover, Munich, Stuttgart, the Mining Schools of Berlin, Clausthal, and Freiberg, and the Agricultural Schools, are almost all well provided with laboratories where researches in pure chemistry are carried on along with studies in applied chemistry. And these institutions are confided to men of proved scientific authority, who make it their task not merely to initiate the young students in the practice of chemistry, but to rouse in them the spirit of research and guide them into the track of discovery.

By means of the influx of foreign students, German science and German ideas are diffused, and at the same time German merchandise and German products. In the years 1891 and 1892 there were not fewer than 446 students of American nationality studying at German Universities; and not fewer than 800 at the Polytechnics, the Mining and Agricultural Colleges of Germany. Shall we reconsider our ways, or shall we go on examining and being examined, until we arrive at a universal collapse such as our Chinese models and forerunners in examinationism have just reached?

CORRESPONDENCE.

BORAX AND STANDARD ACID SOLUTIONS.

To the Editor of the Chemical News.

Sir,—If our method of standardising acid solutions by means of borax is not new, as Mr. Droop Richmond says in Chemical News, vol. lxxii., p. 5, we at least have discovered it independently, and have done something to make it better known.

Our aim was not to show to what accuracy the method could be carried, but rather to point out that, without taking any special precautions, results of very fair accuracy could be obtained.

We do not consider it necessary to estimate the water of crystallisation if *large clear crystals* of borax are used, but as this may be open to question, we intend making further experiments to test this point. The results we obtained were certainly good enough for ordinary analytical work. One of the results is evidently a little incorrect, but probably through no fault of the method employed. We do not know why Mr. Richmond should have dragged carbon dioxide into the question.—We are, &c.,

E. P. Perman.
W. John.

University College, Cardiff,
August 6, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Zeitschrift fur Analytische Chemie.
Vol. xxxiii., Part 6.

(This part has appeared only after vol. xxxiv. has already commenced appearing).

Wine Statistics of Germany. VII.—A continuation of a voluminous report interesting exclusively to the wine trade.

Acid Potassium Tartrate as a Fundamental Substance for Volumetry.—A. Bornträger.—The pure acid tartrate has come into use for standardising alkaline solutions, and is giving satisfaction.

Experiments on the Speed of Filtration of various Solutions.—R. Lezé.—From *Comptes Rendus*, cxiv., p. 1440.

On Pyrometry.—Various constructions have been discussed or proposed by Roberts-Austen (paper at Chicago International Congress, 1883), C. Gabb (*Stahl und Eisen*), Uehling and Steinbart (*Stahl und Eisen*).

A small Air Thermometer for Laboratories.—Lothar Meyer (*Berichte*, xxvi., 1047) proposes a modification, here figured, of Bottomley's thermometer (see *Phil. Mag.*, 1888).

Volumeter for Determining the Volumes of large Samples, especially Soils.—Tacke (*Zeit. Angewandte Chemie*).—Readers are referred to the originals for details.

New Form of Weighing Pipette.—H. Schweitzer.—From the *Journal of the American Chemical Society.*

Self-acting Apparatus for Filtration and for Washing Precipitates with Cold or Hot Water.—P. N. Raikow (*Chemiker Zeitung*).—This paper requires the two accompanying figures.

A Minimum Gas Blast.—Hugo Schiff (*Chemiker Zeitung*).—This paper also cannot be reproduced without the accompanying illustration.

Protective Capsules for Platinum Crucibles.—H. Petrzilka.—The author uses platinum capsules, gilt without, so as to withstand smoking flames, of such a shape and size as to completely cover the bottom of the crucible as far as the flame extends.

Determination of Carbon in Iron.—A conspectus of the most general methods for determining the carbon contained in iron, as proposed by A. Ledebur (*Verein zur Belford. de Gewerb Fleisses*); Regnault, Jüptner, and Gmelin ("Handbuch für Eisenhütten Chemiker"); Sarnström, Ullgren and Elliott, McCreath, Rurüp (*Chemiker Zeitung*); Barba (*Stahl und Eisen*); Langley, Blair, Dudley, and Shimer (*Zeit. Angewandte Chemie, Mining Journal*); Lorenz (*Zeit. Angewandte Chemie*); Woehler, Eggertz, Ukena (*Stahl und Eisen*).

Melting and Boiling Points of the Phenols and their Benzoates.—A. Béhal and E. Choay.—From the *Comptes Rendus*, cxviii., p. 1211.

Determination of Nitrogen.—W. F. Keating Stock.—From the *Analyst*, xviii., 58.

Determination of the Thioureas, and their Separation from the Sulphocyanides. — H. Salkowski (*Berichte*).—In solutions of pure thioureas the total sulphur is precipitated as silver sulphide by ammoniacal silver nitrate. It is filtered off, washed, and heated, first over the simple Bunsen flame, and then fused over the gas blast. All the silver sulphide is thus converted into silver, from the weight of which the quantity of thiourea is calculated. 2 atoms of silver represent 1 mol. of thiourea. For separating thioureas from the sulphocyanides, the clear solution is mixed with an excess of ammoniacal solution of silver. A mixture of silver sulphide and sulphocyanide is precipitated, though a part of the latter remains in solution. After some hours the conversion of the thioureas is completed, when the precipitate is filtered and washed. The filtrate is acidified with sulphuric acid, and the precipitate of silver sulphocyanide is allowed to stand in darkness. The washed precipitate is digested in the cold with solution of potassium cyanide until all the silver sulphocyanide is dissolved. After dilution it is filtered, and the washed silver sulphide is weighed as silver in the manner mentioned above. The filtrate is acidulated with sulphuric acid and heated on the water-bath until all the hydrocyanic acid is expelled. If this is delayed, silver sulphocyanide remains in solution. The silver sulphocyanide thus obtained, along with that which had been set aside in the dark, is filtered on a filter which has been dried at 105°. After filtering and drying at 105° the silver sulphocyanide is weighed.

Detection of the Fat of the Ox in Lard.—W. F. Keating Stock.—From the *Analyst*, xix., 2.

Determination of Hübl's Iodine Number. — W. Fahrion (*Chemiker Zeitung*, xvii., p. 1100).—The author observes that methylic alcohol is preferable to ethylic alcohol for the preparation of Hübl's iodine solution. The solution of sublimate-iodine in methylic alcohol certainly becomes weaker in time, but not to the same extent as the solution in ethylic alcohol. Fahrion shows also that along with the addition of iodine atoms to the double combinations of the non-saturated fatty acids there ensue other processes, so that in general the iodine number is found rather higher than would correspond to the proportion of non-saturated fatty acids in the oil. A high temperature and exposure to light increases the number considerably.

Determination of the Melting-point of Solids.—E. J. Bevan.—From the *Analyst*, xviii., p. 286.

Determination of Fatty Matter in Milk.—The process of Leo Liebermann and S. Szekely has been verified and recommended by Long (*Pharm. Zeitung*).

Arrangemement for a Rapid Approximate Determination of the Quantity and Purity of Carbonic Acid in Mineral Waters, &c.—Th. Kyll (*Zeit. Angew. Chemie*).—Apparently a hollow corkscrew ending in a three-way cock.

Chemistry of Vegetable Fibres.—C. F. Cross, E. J. Bevan, and C. Beadle.—From the CHEMICAL NEWS, lxviii., p. 227.

Examination of the Ethereal Oils.—Schimmel and Co.—A very extensive paper, not suitable for abstraction.

Method for the Volumetric Determination of the Phosphoric Acid, Soluble in Water, contained in Superphosphates.—W. Kalman and K. Meissels.—Already inserted.

Determination of Uric Acid, and of the so-called Xanthine-substances in Urine. — E. Salkowski (*Centralblatt f. Med. Wissenschaft*).—This paper will also be inserted in full.

Detection of Glucose and other Cætohydrates in Urine.—K. Baisch (*Zeit. Physiol. Chemie*).—This paper will also be inserted in full.

Examination of Blood-pigment as to its Absorbent Power for the Violet and Ultra-Violet Rays.—H. Grabe.—Already inserted.

The Atomic Weight of Barium. — T. W. Richards (*Amer. Acad. Arts and Sciences*).—Already inserted.

MISCELLANEOUS.

The Drug and Chemical Trades Exhibition.—We have the pleasure of announcing that, on the 10th, 11th, 12th, and 13th of next month, there will be held in the Royal Agricultural Hall, N. (Islington), an Exhibition of the Drug, Chemical, and Allied Trades. The promoters, subscribers to the *British and Colonial Druggist*, hope to render this demonstration a periodically recurring display, so that it may bring under the notice of the trades and of their customers all improvements, new products, and procedures which may present themselves. The promoters admit that former exhibitions in connection with the drug and chemical trades have not proved successful. On the present occasion the management will not only be entirely new, but a general attendance of the trade is practically guaranteed, and most of the leading firms concerned have already promised their support to the undertaking, and intend to be represented. No department of our national industry and commerce requires to be more energetically and prudently supported than that in question. We hope that enlightened self-interest, not less than patriotism, will combine to ensure the success of the present Exhibition.

Award of the Hodgkins Prize of 10,000 Dollars to Lord Rayleigh and Professor Ramsay.—In March, 1893, it was announced by the Smithsonian Institution, in furtherance of the wishes of Mr. Thomas Hodgkins, who had presented a large donation to the Institution for 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," that a prize of 10,000 dollars would be given for a treatise embodying some new and important discovery in regard to the nature and properties of atmospheric air. The competing treatises had to be sent in before the end of December, 1894. We have much pleasure in announcing that this prize has been awarded to Lord Rayleigh and Professor Ramsay for their treatise on the discovery of Argon.

Clay Filters, and their Use in Chemical and Bacteriological Laboratories.—W. Pukall (*Berichte*).—The author has produced filters which have not the soft sensitive surface of the Chamberland or the Berkefeld (Kieselguhr) filters, but have in a high degree the power of transmitting gases or liquids on the application of exhaustion from below or pressure from above. The filters consist of a suitable composition of china clays of different beds (aluminium silicate with quartz), which can be sharply burnt though remaining sufficiently porous. The construction recommended by Pukall is figured in the original.

THE CHEMICAL NEWS.

VOL. LXXII., No. 1865.

THE SPECTRUM OF HELIUM.

By WILLIAM CROOKES, F.R.S.

IN the CHEMICAL NEWS for March 29th last (vol. lxxi., p. 151) I published the results of measurements of the wave-lengths of the more prominent lines seen in the spectrum of the gas from clèveite, now identified with helium. The gas had been given to me by the discoverer, Professor Ramsay; and being from the first batch prepared, it contained other gases as impurities, such as nitrogen and aqueous vapour, both of which gave spectra interfering with the purity of the true helium spectrum. I have since, thanks to the kindness of Professors Ramsay and J. Norman Lockyer, had an opportunity of examining samples of helium from different minerals and of considerable purity as far as known contamination is concerned. These samples of gas were sealed in tubes of various kinds and exhausted to the most luminous point for spectrum observations. In most cases no internal electrodes were used, but the rarefied gas was illuminated solely by induction, metallic terminals being attached to the outside of the tube.* For photographic purposes, a quartz window was attached to the end of the tube, so that the spectrum of the gas could be taken "end on."

My examinations have chiefly been made on five samples of gas.

1. A sample from Professor Ramsay in March last. Prepared from Clèveite.
2. A sample from Professor Ramsay in May last. Prepared from a specimen of Uraninite sent to him by Professor Hillebrand. Gas obtained by means of sulphuric acid; purified by sparking.
3. A sample from Professor Ramsay in June last. Prepared from Bröggerite.
4. A sample from Professor Lockyer in July last. Prepared by a process of fractional distillation from a sample of Bröggerite sent to him by Professor Brögger.
5. A sample of gas from Professor Ramsay, "Helium Purissimum." This was obtained from mixed sources, and had been purified to the highest possible point.

In the following table the first four samples of gas will be called:—1. "Clèveite, R."; 2. "Uraninite, R."; 3. "Bröggerite, R."; and 4. "Bröggerite, L." Only the strongest of the lines, and those about which I have no doubt, are given. The wave-lengths are on Rowland's scale.

The photographs were taken on plates bent to the proper curvature for bringing the whole spectrum in accurate focus at the same time. The spectrum given by a spark between an alloy of equal atoms of mercury, cadmium, zinc, and tin, was photographed at the same time on the plate, partially overlapping the helium spectrum; suitable lines of these metals were used as standards. The measurements were taken by means of a special micrometer reading approximately to the 1/100,000th inch, and with accuracy to the 1/10,000th of an inch. The calculations were performed according to Sir George Stokes's formula, supplemented by an additional formula kindly supplied by Sir George Stokes, giving a correction to be applied to the approximate wave-lengths given by the first formula, and greatly increasing the accuracy of the results.

Wave-length.	Intensity.	
7065·5	5	A red line, seen in all the samples of gas. Young gives a chromospheric line at 7065·5.
6678·1	8	A red line, seen in all the samples of gas. Thalén gives a line at 6677 and Lockyer at 6678. Young gives a chromospheric line at 6678·3.
5876 0	30	The characteristic yellow line of helium, seen in all the samples of gas. Thalén makes it 5875·9, and Rowland 5875·98. Young gives a chromospheric line at 5876.
5062·15	3	
5047·1	5	A yellow-green line, only seen in "Helium Puriss." and in "Bröggerite, R," and "L." Thalén gives the wave-length as 5048.
5015·9	7	A green line seen in all the samples of gas. Thalén gives the wave-length 5016. Young gives a chromospheric line at 5015·9.
4931·9	3	
4922·6	10	A green line, seen in all the samples of gas. Thalén gives the wave-length 4922. Young gives a chromospheric line at 4922·3.
4870·6	7	A green line, only seen in "Uraninite, R." Young gives a chromospheric line at 4870·4.
4847·3	7	A green line, only seen in "Uraninite, R." Young gives a chromospheric line at 4848·7.
4805·6	9	A green line, only seen in "Uraninite, R." Young gives a chromospheric line at 4805·25.
4764·4	2	There is a hydrogen line at 4764·0.
4735·1	10	A very strong greenish blue line, only seen in "Uraninite, R."
4713·4	9	A blue line, seen in all the samples of gas. Thalén's measurement is 4713·5. Young gives a chromospheric line at 4713·4.
4658·5	8	A blue line, only seen in "Uraninite, R."
4579·1	3	A faint blue line, seen in "Uraninite, R." Lockyer gives a line at 4580, from certain minerals. I can see no traces of it in the gas from Bröggerite. A hydrogen line occurs at 4580·1.
4559·4	2	Young gives a chromospheric line at 4558·9.
4544·1	5	
4520·9	3	A faint blue line, seen in "Uraninite, R." Lockyer gives a line at 4522, seen in the gas from some minerals. Young gives a chromospheric line at 4522·9. It is absent in the gas from Bröggerite.
4511·4	5	A blue line, seen in "Uraninite, R," but not in the others. It is coincident with the strong head of a carbon band in the CO_2 and Cy spectrum.
4497·8	2	There is a hydrogen line at 4498·75.
4471·5	10	A very strong blue line, having a fainter line on each side, forming a close triplet. It is a prominent line in all the samples of gas examined. Young gives the wave-length 4471·8 for a line in the chromosphere,. and Lockyer gives 4471 for a line in gas from Bröggerite.
4435·7	9	Seen in "Helium Puriss."
4437·1	1	Young gives a chromospheric line at 4437·2.

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* *Journal of the Institution of Electrical Engineers*, Part 91, vol. xx., Inaugural Address by the President, William Crookes, F.R.S., Jan. 15th, 1891.

Wave-length.	Intensity.	
4428·1	10	These two lines form a close pair. I can only see them in "Uraninite, R." No trace of them can be seen in the gases from other sources. Young gives chromospheric lines at 4426·6 and 4425·6.
4424·0	10	
4399·0	10	A strong line, only seen in "Uraninite, R." Absent in the gas from the other sources. Lockyer gives a line at 4398 in gas from certain minerals. Young gives a chromospheric line at 4398·9.
4386·3	6	Seen in all the samples of gas. Young gives a chromospheric line at 4385·4.
4378·8	8	These two lines form a pair seen in "Uraninite, R," but entirely absent in the others.
4371·0	8	
4348·4	10	Seen in "Uraninite, R." Lockyer finds a line at 4347 in the gas from certain minerals.
4333·9	10	Probably a very close double line. Seen in "Uraninite, R" and "Clèveite, R." Not seen in the other samples. Lockyer gives a line in the gas from certain minerals at 4338.
4298·7	6	Only seen in "Uraninite, R." Young gives a chromospheric line at 4298·5.
4281·3	5	Only seen in "Uraninite, R."
4271·0	5	Only seen in "Uraninite, R." The strong head of a nitrogen band occurs close to this line.
4258·8	7	Seen in all the samples of gas.
4227·1	5	Only seen in "Uraninite, R." Young gives a chromospheric line at 4226·89.
4198·6	9	These three lines form a prominent group in "Uraninite, R," they are very faint in "Clèveite, R," and in "Bröggerite, L," but are not seen in "Bröggerite, R."
4189·9	9	
4181·5	9	
4178·1	1	An extremely faint line. Lockyer gives a line at 4177, seen in the gas from certain minerals, and Young gives a chromospheric line at 4179·5.
4169·4	6	Seen in "Helium Puriss."
4157·6	8	A strong line in "Uraninite, R," very faint in "Bröggerite, R," and "L," not seen in "Clèveite, R."
4143·9	7	Strong in "Clèveite, R," in "Helium Puriss.," and in "Bröggerite, L." It is faint in "Uraninite, R," and not seen in "Bröggerite, R." Lockyer gives a line at 4145 in gas from certain minerals.
4121·3	7	Present in all the gases except "Clèveite, R."
4044·3	9	Present in "Uraninite, R," and "Clèveite, R." Absent in the others.
4026·1	10	These lines form a very close pair, seen in all the samples of gas, except "Bröggerite, R." Lockyer finds a line in Bröggerite gas at 4026·5.
4024·15	6	
4012·9	7	Seen in all the samples of gas.
4009·2	7	Seen in "Helium Puriss."
3964·8	10	The centre line of a dense triplet. Only seen in "Clèveite, R," in "Helium Puriss.," and "Bröggerite, L." Hale gives a chromospheric line at 3964.
3962·3	4	Seen in all the samples of gas.
3948·2	10	Very strong in "Uraninite, R," very faint in "Clèveite, R," and not seen in the others. Lockyer finds a line in gas from Bröggerite at 3947. There is an eclipse line at the same wave-length.
3925·8	2	Seen in "Helium Puriss."
3917·0	2	Seen in "Helium Puriss."
3913·2	4	Only seen in "Uraninite, R," and "Helium Puriss." Hale gives a chromospheric line at 3913·5.
3890·5	9	A very strong triplet, seen in all the samples of gas. Lockyer finds a line having a wave-length 3889 in gas from Bröggerite. Hale gives a chromospheric line at 3888·73. There is a strong hydrogen line at 3889·15.
3888·5	10	
3885·9	9	
3874·6	6	Only seen in "Uraninite, R."
3867·7	8	Seen in "Helium Puriss."
3819·4	10	Seen in all the samples of gas. Deslandres gives a chromospheric line at 3819·8.
3800·6	4	Seen in "Helium Puriss."
3732·5	5	Seen in "Helium Puriss." Hale gives a chromospheric line at 3733·3.
3705·4	6	Seen in all the samples of gas. Deslandres gives a chromospheric line at 3705·9.
3642·0	8	Only seen in "Uraninite, R."
3633·3	8	Seen in "Helium Puriss."
3627·8	5	Only seen in "Uraninite, R."
3613·7	9	Seen in "Helium Puriss."
3587·0	5	Seen in "Helium Puriss."
3447·8	8	Seen in "Helium Puriss."
3353·8	5	Seen in "Helium Puriss."
3247·5	2	Seen in "Helium Puriss."
3187·3	10	The centre line of a close triplet. Very faint in "Clèveite, R," and "Uraninite, R," and strong in "Helium Puriss." and in "Bröggerite, L." It is not seen in "Bröggerite, R."
2944·9	8	A prominent line, only seen in "Helium Puriss." and in "Bröggerite, L."
2536·5	8	Seen in "Helium Puriss." A mercury line occurs at 2536·72.
2479·1	4	Seen in "Helium Puriss."
2446·4	2	Seen in "Helium Puriss."
2419·8	2	Seen in "Helium Puriss."

Some of the more refrangible lines may possibly be due to the presence of a carbon compound with the helium. To photograph them a long exposure, extending over several hours, is necessary. The quartz window has to be cemented to the glass with an organic cement, and the long-continued action of the powerful induction current on the organic matter decomposes it, and fills the more refrangible end of the spectrum with lines and bands in which some of the flutings of hydrocarbon, cyanogen, and carbonic anhydride are to be distinguished.

There is a great difference in the relative intensities of the same lines in the gas from different minerals. Besides the case mentioned by Professor Kayser of the yellow and green lines, 5876 and 5016, which vary in strength to such a degree as to render it highly probable that they represent two different elements, I have found many similar cases of lines which are relatively faint or absent in gas from one source and strong in that from another source.

Noticing only the strongest lines which I have called "Intensity 10," "9," or "8," and taking no account of them when present in traces in other minerals, the following appear to be special to the gas from uraninite:—

4735·1
4658·5
4428·1
4424·0
4399·0
4378·8
4371·0
4348·4
4198·6
4189·9
4181·5
4157·6
3948·2
3642·0

The following strong lines are present in all the samples of gas :—

7065·5
6678·1
5876·0
5015·9
4922·6
4713·4
4471·5
4386·3
4258·8
4012·9
3962·3
3890·5
3888·5
3885·9
3819·4
3705·4

The distribution assigned to some of the lines in the above Tables is subject to correction. The intensities are deduced from an examination of photographs, taken with very varied exposures; some having been exposed long to bring out the fainter lines, and some a short time to give details of structure in the stronger lines. Unless all the photographs have been exposed for the same time, there is a liability of the relative intensities of lines in one picture not being the same as those in another picture. Judgment is needed in deciding whether a line is to have an intensity of 7 or 8 assigned to it; and as in the Tables I have not included lines below intensity 8, it might happen that another series of photographs with independent measurements of intensities would in some degree alter the above arrangement.

In the following Table I have given a list of lines which are probably identical with lines observed in the chromosphere and prominencies :—

Wave-lengths observed of helium.	Intensities.	Wave-lengths of chromospheric lines,* Rowland's scale.
7065·5	10	7065·5
6678·1	10	6678·3
5876·0	30	5876·0
5015·6	6	5015·9
4922·6	10	4922·3
4870·6	7	4870·4
4847·3	7	4848·7
4805·6	9	4805·25
4713·4	9	4713·4
4559·4	2	4558·9
4520·9	3	4522·9
4471·5	10	4471·8
4437·1	1	4437·2
4428·1	10	4426·6
4424·0	10	4425·6
4399·0	10	4398·9
4386·3	6	4385·4
4298·7	6	4298·5
4227·1	5	4226·89
4178·1	1	4179·5
3964·8	10	3964·0 H.†
3948·2	10	3945·2 H.
3913·2	4	3913·5 H.
3888·5	10	3888·73 H.
3819·4	10	3819·8 D.
3732·5	5	3733·3
3705·4	6	3705·9 D.

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* "A Treatise on Astronomical Spectroscopy," by Dr. J. Scheiner, translated by E. B. Frost, Boston, 1894.

† The wave-lengths to which the initials D. and H. are added are wave-lengths of lines photographically detected in the spectrum of the chromosphere by Deslandres (D) and Hale (H). Their photographs do not extend beyond wave-length 3630. Professor Lockyer (*Roy. Soc. Proc.*, vol. lviii., p. 116, May, 1895) has already pointed out fourteen coincidences between the wave-lengths of lines in terrestrial helium and in those observed in the chromosphere, the eclipse lines, and stellar spectra.

NOTE ON HELIUM AND ARGON.

By Prof. H. KAYSER, of Bonn.

Hitherto helium has been found only in a few minerals, and we do not know as yet in what state it exists there. It may therefore be interesting that I have found it in a free state in Nature. Some time ago I received information that in the springs of Wildbad, in the Black Forest, bubbles of gas rise up which—according to an old analysis of Fehling—contain about 96 per cent of nitrogen. As in all such cases it is possible that considerable quantities of argon may be found, I submitted the gas to analysis. About 430 c.c. were mixed with oxygen, and sparks were caused to strike through it in presence of potassa-lye. The excess of oxygen was then removed by means of potassium pyrogallate. After desiccation there remained 9 c.c., which were filled into Geissler tubes for a spectroscopic examination of the gas. It showed the lines of argon and helium, the latter not in a small quantity, as its lines appeared very bright and could be readily photographed. Runge and Paschen have found that the gas evolved from clèveite and bröggerite is a mixture of two substances, one of which, helium, is most highly represented in the visible spectrum by the yellow line D_3, whilst the other, not as yet named, is represented by the green line $\lambda = 501{\cdot}6\ \mu\mu$. Both these elements are also represented in the Wildbad gas, though it seems to me that the second element is here in a smaller proportion than in bröggerite, as the green line is relatively feebler.

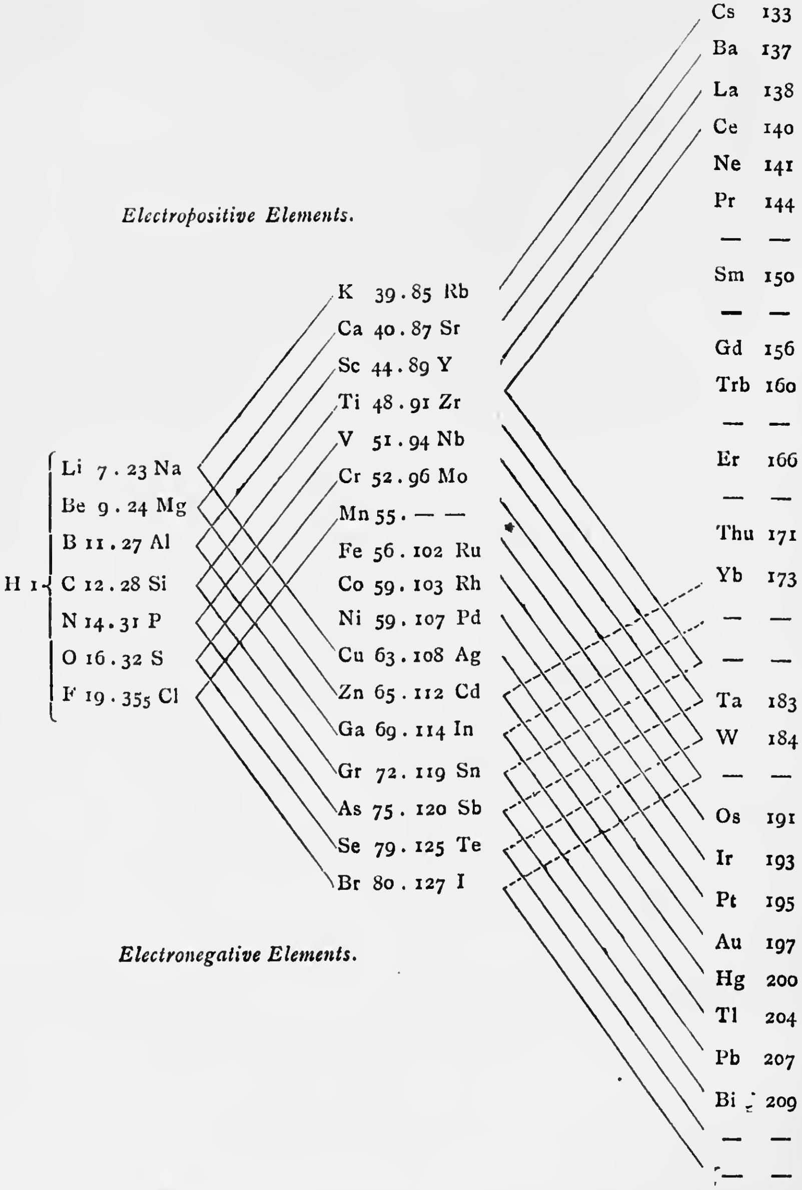
In this result it seems to me especially interesting that thus for the first time a place has been discovered where the two gases included under the name "helium" are liberated and stream out into the atmosphere. Hence free helium must be found in the air along with argon. In fact, I have found in Geissler tubes which I had personally filled with the purest argon possible,—and that at a time when I had not yet worked with helium, so that no admixture with it could have occurred in my laboratory, — on direct comparison with helium tubes the presence of D_3 in the argon spectrum; and I have obtained photographically the strong lines at $388{\cdot}9\ \mu\mu$. The lines are certainly very faint, but I consider the presence of helium in the air of Bonn as beyond any doubt. Whether this presence of gases in the springs of Wildbad has any connection with their hygienic efficacy, and whether the gases occur in similar springs, the future must show.

Bonn, August 10, 1895.

SYSTEMATIC ARRANGEMENT OF THE CHEMICAL ELEMENTS.

By JULIUS THOMSEN.

After D. Mendeleeff and Lothar Meyer, twenty-six years ago, had represented the properties of the chemical elements as a periodic function of the atomic weights, the attempt was made to arrange the elements in a somewhat different manner, so that their periodicity might come to light as completely as possible. The original form which both Mendeleeff and Meyer employed in their tables for the exposition of periodicity contained the elements distributed in groups of seven members (partly, also, of ten members), and the tables contained eleven such groups. But it soon appeared that this division of the entire number of elements did not present the desired periodicity in a fully satisfactory manner, and the tables were modified in such a manner that only the two first groups retained each the number of seven members, whilst the remaining elements were arranged in five groups each of seventeen members, but of these groups only the two first were approximately complete. But this form also had considerable defects; it is especially difficult to find for



the elements of the numerous rare earths a place suitable to the character of the entire system, since these substances are closely connected, and their atomic weight fall very near together.

The arrangement which I have used, and which is given in the following table, seems to me more satisfactory.

Few words only are needful to explain the significance of this arrangement. Hydrogen, as usual, forms the head of the table. The other elements are divided into three main groups, of which the first contains 2 + 7 elements, the second 2 + 17, and the third 31 elements; after which, then, probably follows a corresponding series of 31 elements, of which, as yet, only two elements are known (thorium and uranium).

The first two groups, each containing two series, quite correspond to the arrangement now customary. But the table shows an essential difference in the collocation of the remaining elements in one series, beginning with electropositive cæsium and concluding with the metals corresponding to the electronegative members, hitherto known only as far as bismuth. A division of the elements of this group into two more classes is not possible if we wish to carry out the character of the entire arrangement according to valence and electrical character.

The table shows in perspicuous manner the relationship of the elements. From hydrogen the lines connecting the kindred elements lead, on the one hand, to the electropositive lithium, and, on the other, to electronegative fluorine, and between these two members the other two members of the first series arrange themselves in the known manner. The members of the second series of the first group connect also in a known manner, each to a kindred member of the first; but in the transit from the second to the third series, *i.e.*, from the first to the second group, the division already observed in hydrogen repeats itself, each member of the second series being related to the members of the third; that is, with one member belonging to the electropositive part and another belonging to the electronegative part of the third series. Thus, sodium is related to potassium and copper, magnesium to calcium and zinc, aluminium to scandium and gallium, &c., and, lastly, chlorine with manganese and bromine. There then remain three members of the third series (iron, cobalt, and nickel), which form the transition from manganese to copper.

The fourth series connects itself in a known manner to the third, just as in the first group the second series connects itself to the first. On the transition from the second to the third group a similar behaviour takes place as on the transit from the second to the third. Hence, also, the affinity of the elements appears to be demonstrable in two directions; partly in an electropositive and partly in an electronegative direction. Just as we are led from silicon of the first group on the one hand to titanium, and on the other to germanium of the second group, so pass the lines of affinity between the second and third group, *e.g.*, from zirconium on the one hand to cerium with the atomic weight 140, and on the other hand to an element not definitely determined, with an atomic weight of about 181. Between these two elements are grouped a great number of elements corresponding to the rare earths which all display a close relation, as also the intermediate elements of the third series from manganese to zinc.

Many of the elements of the fifth series have only been partially investigated, and their nearest affinities in the fourth series cannot be indicated with certainty; yet we see various analogies among the better known elements. The table gives an indication, by means of dotted lines, such as that of cadmium and ytterbium (known by the peculiar formula of the sulphate).

The atomic weights in the table are carried to the nearest whole numbers, and are merely to serve as guides.

Of the elements of the rare earths, I have included in the table all contained in the table of atomic weights published by F. W. Clarke (*Journ. Amer. Chem. Soc.*, 1894, xvi., 3).

Finally, I wish to draw attention to a curious fact, *i.e.*, that the number of elements in the single series, 1, 7, 17, and 31, may be expressed by $1+2 \cdot 3+2 \cdot 5+2 \cdot 7$. Probably this occurrence of the prime numbers 1, 3, 5, 7, is merely accidental.

Although the table here given differs from the customary tables only in its arrangement, I believe that it presents in a very perspicuous manner the facts which may be deduced from the periodic system.—*Zeitschrift für Anorg. Chemie*, ix., p. 190.

QUANTITATIVE SEPARATION OF METALS IN ALKALINE SOLUTION, BY MEANS OF HYDROGEN PEROXIDE.

By P. JANNASCH and H. KAMMERER.

1. *Separation of Manganese and Silver.*

For separating these two metals we put into a small beaker 0·7 to 0·8 grm. silver nitrate and an equal quantity of manganese-ammonium sulphate, with 10 c.c. concentrated nitric acid and the same volume of water. The solution is poured into a mixture of 20 c.c. water, 50 hydrogen peroxide, and 40 concentrated ammonia, and the whole is covered and heated upon the water-bath for ten to twelve minutes, whereupon the precipitate of hydrated manganese peroxide, which rapidly deposits, is filtered off. The precipitate is most carefully washed, firstly with a mixture of 8 parts by volume of water, 17 of hydrogen peroxide, and 17 of strong ammonia, and finally with hot water, incinerated, and lastly ignited before the blast until the weight is constant. The filtrate, containing all the silver, is heated on the water-bath until the ammoniacal odour disappears, acidified with concentrated nitric acid, and the silver is separated as chloride in the ordinary manner.

The separation of manganese and silver proceeds extremely easily and smoothly. A single precipitation of the manganese is perfectly sufficient, as the precipitate on examination was found perfectly free from traces of silver. In more complicated mixtures, *e.g.*, an alloy of silver, bismuth, manganese, and nickel, the new process is decidedly to be preferred to a preliminary precipitation of the silver.

2. *Separation of Bismuth and Cobalt.*

As our initial material we used cobalt-ammonium sulphate and pure metallic bismuth. About 0·5 grm. of the cobalt salt and 0·35 grm. bismuth are heated in a crucible upon the water-bath with 10 c.c. concentrated nitric acid and 10 c.c. water until dissolved. In a second large porcelain capsule we have in readiness a mixture of 20 c.c. water, 50 hydrogen peroxide, and 50 concentrated ammonia, into which we pour the metallic solution after the addition of 10 c.c. concentrated nitric acid. After subsidence the bismuth precipitate (still including traces of cobalt) is filtered off, and washed first with a mixture of hydrogen peroxide and ammonia, as above, then with dilute ammonia (1 : 2), and lastly with hot water. When this has been thoroughly done the precipitate is dissolved on the filter with hot dilute nitric acid (1 : 3), noting the quantity thus consumed, and then add to the cold bismuth solution so much concentrated nitric acid that 20 c.c. of it may again be present in the liquid. The bismuth is then precipitated a second time exactly as before, the precipitate washed precisely as above, dried at 90°, incinerated, and weighed as bismuth oxide in a platinum crucible.

The precipitate, containing all the cobalt, is dried perfectly on the water-bath, and then heated strongly in a large nickel air-bath until all the ammonium salts are expelled. The residual cobalt salt is now taken up with a little hot water, to which a few drops of hydrochloric acid and a little hydrogen peroxide have been added, diluted to at most 100 c.c., and finally precipitated at a boiling heat with a slight excess of pure soda, with the simultaneous addition of some bromine. The precipitate obtained is well washed, dried, incinerated (the filter separately), and weighed as cobalti-cobaltous oxide. Or the cobalt may be directly precipitated from the original ammoniacal solution with ammonium sulphide. This precipitate must be heated for some time on the water-bath until completely deposited, when it is filtered and washed with hot water containing ammonium sulphide. By the use of warm dilute aqua regia alternately with hydrogen peroxide, it is easily practicable to re-dissolve the sulphide for the precipitation of the cobalt with soda and bromine.—*Berichte*, 1895, No. 11, p. 1407.

DETERMINATION OF SMALL QUANTITIES OF ARSENIC.

By AD. CARNOT.

We possess already numerous methods for the determination of arsenic; but these procedures, if convenient for large proportions, leave much to be desired in the case of slight quantities. But in a number of instances it is important to determine the latter with accuracy. We know, for instance, that various metals—copper, iron, nickel, &c.—lose in part their industrial value if they contain a proportion of arsenic amounting to one part in a thousand. Great precision is also necessary for the determination of arsenic in mineral waters, where it sometimes plays a most important part, although its proportion scarcely ever attains some tenths of a m.grm. per litre.

The method which I am about to explain consists in precipitating the arsenic in the state of sulphide, transforming the latter into arsenic acid by means of ammonia, silver nitrate, and hydrogen peroxide. The arsenic acid is then determined as bismuth arseniate, a compound very insoluble in dilute nitric acid, the weight of which is nearly five times equal to that of the element to be determined.

The first operation is almost always the necessary complement of the treatment required for isolating the arsenic from other substances. According to the cases, the precipitation of the arsenic is effected either by the action of sulphuretted hydrogen upon an acid solution where it is present as arsenious or arsenic acid, or by the decomposition by means of an acid of a solution in which the arsenic is present as a sulpho-salt. Hence the precipitate is composed of a more or less important quantity of free sulphur.

This mixture, after having been well washed, is treated with hot ammoniacal water; this readily dissolves the arsenic sulphide, leaving on the filter nearly all the free sulphur; the surplus will be precipitated by the following operation:—We pour into the solution a sufficiency of silver nitrate, which produces a precipitate of silver sulphide, and at the same time ammonium arsenite or arseniate, according as the precipitate contained arsenic trisulphide or pentasulphide. For the trisulphide, *e.g.*, the transformation is represented by the following equation:—

$$As_2S_3+3Ag_2O.N_2O_5=3Ag_2S+As_2O_3+3N_2O_5.$$

It is heated with stirring for some minutes to collect the precipitated sulphide, and we satisfy ourselves that the liquid is not rendered turbid by a furher addition of a silver salt. We then add a few drops of pure hydrogen peroxide (or at least containing no other acid than the hydrochloric), which is without action on silver sulphide, but which, at once, in presence of an excess of ammonia, converts arsenious acid into arsenic acid.

We heat again to near 100°, until the odour of ammonia has totally disappeared, and we add a few drops of nitric acid so as to slightly acidify the liquid. We thus re-dissolve any silver arseniate which has been deposited on the expulsion of the ammonia, and we precipitate in the state of silver chloride all the chlorine which may be derived from an imperfect washing of the arsenic sulphide at the outset, or from an impurity in the hydrogen peroxide employed.

We collect on a filter the precipitates of silver sulphide and chloride, and, after washing, pour into the filtrate a nitric solution of bismuth subnitrate, containing at least five or six times as much of this reagent as there may be arsenic in the substance under analysis.

We saturate with ammonia, and allow to boil for some minutes. The white precipitate of bismuth hydroxide and arseniate is allowed to subside, and the liquor is decanted through a small tared filter. The precipitate on the filter and in the flask is then dissolved by water containing 1/15th of its volume of nitric acid at 1·310, and the solution is caused to boil. This degree of dilution is the most suitable for gradually dissolving the bismuth hydroxide and leaving the arseniate completely insoluble. There is formed a heavy crystalline precipitate, which is collected on the small tared filter, and washed first with water acidulated to $\frac{1}{15}$, and then with pure water. It is dried at 110°, and weighed.

The analysis of the precipitate leads to the formula—

$$As_2O_5Bi_2O_3 + H_2O.$$

It contains, therefore, in 100 parts, 21·067 of arsenic, or 32·303 parts of arsenious acid. The precipitate must be weighed, dried, and not ignited, on account of the losses produced at a red-heat by the reductive action of the paper. A series of experiments prove that this method is very certain and accurate.—*Comptes Rendus*, cxxi., 20.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending July 31st, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, August 12th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 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 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 189 samples examined one was recorded as "slightly turbid," and one as "clear, but dull;" the remainder were clear, bright, and well filtered.

July has been the wettest month since November last, when an excess of 2·49 inches of rain fell in the Thames valley. The actual amount of rain during the month just passed was 3·41 inches, and as the mean of 25 years is 2·58 there has fallen an excess of 0·83 inch. With the exception of a heavy storm on the 1st, the first half of July was dry; after the 1st scarely any rain fell till the 18th, the greater part falling between the 18th and 25th.

The high level of purity of the Thames-derived waters, to which we drew attention in the report for June, was sustained in July, notwithstanding the fact that turbidity and peaty colouring-matters are always washed from the land into a river by heavy rain following a drought. A comparison of the chemical composition of the waters in July and in June shows that the constituents are almost identical in quantity.

We have continued to examine the samples drawn from the clear water wells of the water companies at their works, and from the unfiltered river water. The unfiltered Thames water contained an average of 3425, and the filtered water at the works contained 30 microbes per cubic centimetre.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

THE VOLUMETRIC ESTIMATION OF NICKEL

By THOMAS MOORE.

In a former number of the Chemical News (lix., 160, 293) I described a volumetric method for the now industrially important metal nickel. A great many assays made by this process amply proved its reliability, and in this communication it is proposed to describe a modification by means of which it is rendered one of the most exact processes in analytical chemistry. Those chemists who have employed the original method must have noticed that its weak place lay in the use of cupric ferrocyanide as indicator; this, however, is now dispensed with, and argentic iodide substituted. The principles upon which the process depends may be thus described:—If to an ammoniacal solution of nickel containing AgI in suspension (argentic iodide being almost insoluble in weak ammonia) there is added potassic cyanide, the solution will remain turbid so long as all the nickel is not converted into the double cyanide of nickel and potassium, the slightest excess of cyanide being indicated by the clearing up of the liquid, and, furthermore, this excess may be exactly determined by adding a solution of silver until the turbidity is reproduced. It is a fortunate circumstance that the complicated side-reactions existing in Parke's copper assay do not appear to take place with nickel solutions, at least not when the temperature is kept below 20° C. This is fully borne out by the fact that the potassic cyanide may be standardised on either silver or nickel solutions with equal exactness. In practice it has been found best to proceed in the following manner:—

Solution of argentic nitrate, containing about 3 grms. of silver per litre. The strength of this solution must be known with as much accuracy as possible.

Potassic iodide, 10 per cent solution.

Potassic cyanide, 22 to 25 grms. per litre. This solution must be tested every few days, owing to its liability to change.

Standardising the Cyanide Solution.

This may be accomplished in two ways: (*a*) on a solution of nickel of known metallic contents, or (*b*) on the argentic nitrate solution.

(*a*). First accurately establish the relation of the cyanide to the silver solution, by running into a beaker glass 3 or 4 c.c. of the former; dilute this with about 150 c.c. of water, render slightly alkaline with ammonia, and then add a few drops of the potassic iodide. Now carefully run in the silver solution until a faint permanent opalescence is produced, which is finally caused to disappear by the further addition of a mere trace of cyanide. The respective volumes of the silver and cyanide solutions are then read off, and the equivalent in cyanide of 1 c.c. silver solution calculated. A solution containing a known quantity of nickel is now required. This must have sufficient free acid present to prevent the formation of any precipitate, on the subsequent addition of ammonia to alkaline reaction; if this is not so, a little ammonic chloride may be added. A carefully measured quantity of the solution is then taken, containing about 0·1 grm. of nickel, and rendered distinctly alkaline with ammonia, a few drops of potassic iodide added, and the liquid diluted to 150 to 200 c.c. A few drops of the silver solution are now run in, and the solution stirred to produce a uniform turbidity. The solution is now ready to be titrated with the potassic cyanide, which is added slowly and with constant stirring until the precipitate wholly disappears; a few extra drops are added, after which the beaker glass is placed under the argentic nitrate burette, and this solution gently dropped in until a faint permanent turbidity is again visible; this is now finally caused to dissolve by the mere fraction of a drop of the cyanide. A correction must now be applied for the excess of the cyanide added, by noting the amount of silver employed, and working out its value in cyanide from the data already found; this excess must then be deducted, the corrected number of c.c. being then noted as equivalent to the amount of nickel employed.

(*b*). Having determined the relative value of the potassic cyanide to the argentic nitrate, and knowing accurately the metallic contents of the latter, then $Ag \times 0{\cdot}27196$ gives the nickel equivalent. This method is quite as accurate as the direct titration.

A modification of the above process, whereby one burette only is necessary, has been found very convenient, and has given most excellent results. It is based on the following:—When a solution of potassic cyanide, containing a small quantity of argentic cyanide dissolved in it, is added to an ammoniacal solution of nickel containing potassic iodide, it is seen that argentic iodide is precipitated, and the turbidity thus caused in the solution continues to increase up to the point where the formation of the nickelo-potassic cyanide is complete; any further addition after this stage is reached will produce a clearing up of the liquid, until, at last, the addition of a single drop causes the precipitate to vanish. This final disappearance is most distinct, and leaves no room for doubt. Such a solution may be prepared by dissolving 20 to 25 grms. potassic cyanide in a litre of water, adding to this about 0·25 grm. argentic nitrate previously dissolved in a little water. For large quantities of nickel the quantity of silver may advantageously be diminished, and *vice versâ*. The value of the cyanide is best ascertained in the manner already described, on a nickel solution.

Small quantities of cobalt do not seriously affect the results, but it must be remembered that it will be estimated along with the nickel; its presence is at once detected by the darkening of the solution. Manganese or copper render the process valueless, so also does zinc; the latter, however, in alkaline pyrophosphate solution exercises no influence. In the presence of alumina, magnesia, or ferric oxide, citric acid, tartaric acid, or pyrophosphate of sodium may be employed to keep them in solution. The action of iron is somewhat deceptive, as the solution, once cleared up, often becomes troubled again on standing for a minute; should this occur, a further addition of cyanide must be given until the liquid is rendered perfectly limpid. The temperature of the solution should never exceed 20° C.; above this the results become irregular. The amount of free ammonia has also a disturbing influence; a large excess hinders or entirely prevents the reaction; the liquid should, therefore, be only slightly but very distinctly alkaline. A word of caution must be given regarding the potassic cyanide, as many of the reputed pure samples are very far from being so. The most hurtful impurity is, however, sulphur, as it gives rise to a darkening of the solution, owing to the formation of the less readily soluble argentic sulphide; to get rid of the sulphur impurity it is necessary to thoroughly agitate the cyanide liquor with oxide of lead, or, what is far more preferable, oxide of bismuth.

As regards the exactness of the methods, it is unnecessary to give an array of figures. This much, however, may be said, that, after a prolonged experience, extending over many thousands of estimations, they have been found to be more accurate and reliable than either the electrolytic or gravimetric methods, and when time is a consideration the superiority is still more pronounced. The employment of organic acids or sodic pyrophosphate in the case when iron, zinc, &c., are present, allows us to dispense with the tedious separation which their presence otherwise entails; and this is a matter of considerable importance in the assay of nickel mattes or German silver.

Nouméa, New Caledonia.

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.*

By F. W. CLARKE.

To the Members of the American Chemical Society:

Your Committee upon Atomic Weights respectfully submits the following report, which summarises the work done in this department of chemistry during 1894. Although the volume of completed determinations is not large, it is known that several important investigations are in progress, from which valuable results may be expected in the near future. It is in this country that the

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* From the *Journal of the American Chemical Society*, vol. xvii., No. 3. Read at the Boston Meeting, Dec. 28, 1894.

greateat activity exists, and that the greatest progress is being made at present; and the preparation of these reports is therefore a peculiarly appropriate function of the Society. The data for 1894 are as follows:—

The H : O ratio.—An interesting attempt at the indirect measurement of this ratio, which is the base line upon which our system of atomic weights depends, has been made by Julius Thomsen (*Zeit. Phys. Chem.*, xiii., 398). His determinations are really determinations of the ratio $NH_3 : HCl$, and were conducted thus:—First, pure dry gaseous hydrochloric acid was passed into a weighed absorption apparatus containing pure distilled water. After noting the increase in weight, gaseous ammonia was passed throught to slight excess, and the apparatus was weighed again. The excess of ammonia was then measured by titration with standard hydrochloric acid. In weighing, the apparatus was tared by another as nearly like it as possible, containing the same amount of water, Three sets of weighings were made, with apparatus of different size, and these Thomsen considers separately, giving the greatest weight to the experiments involving the largest masses of material. The data are as follows, with the ratio $\frac{HCl}{NH_3}$ in the third column.

First Series.

Wt. HCl.	Wt. NH_3.	Ratio.
5·1624	2·4120	2·1403
3·9425	1·8409	2·1416
4·6544	2·1739	2·1411
3·9840	1·8609	2·1409
5·3295	2·4898	2·1406
4·2517	1·9863	2·1405
4·8287	2·2550	2·1414
6·4377	3·0068	2·1411
4·1804	1·9528	2·1407
5·0363	2·3523	2·1410
4·6408	2·1685	2·1411

Second Series.

Wt. HCl.	Wt. NH_3.	Ratio.
11·8418	5·5302	2·14130
14·3018	6·6808	2·14073
12·1502	5·6759	2·14067
11·5443	5·3927	2·14073
12·3617	5·7733	2·14118

Third Series.

Wt. HCl.	Wt. NH_3.	Ratio.
19·3455	9·0360	2·14094
19·4578	9·0890	2·14081

From the sums of the weights Thomsen finds the ratio to be 2·14087, or 2·13934 in vacuo. From this, using Ostwald's reduction of Stas's data for the atomic weights of nitrogen and chlorine, he gets the ratio—

O : H : : 16 : 0·99946,

or almost exactly 16 : 1. In a later paper (*Zeit. Phys. Chem.*, xiii., 726), Thomsen himself re-calculated Stas's data, with O = 16 as the basis of computation, and derives from them the subjoined values for the elements which Stas studied:—

Ag	107·9299
Cl	35·4494
Br	79·9510
I	126·8556
S	32·0606
Pb	206·9042
K	39·1507
Na	23·0543
Li	7·0307
N	14·0396

Combining these values for chlorine and nitrogen with his ratio $HCl : NH_3$ he gets O : H : : 16 : 0·9992. This, however, is only an apparent support of Prout's hypothesis, for it depends on the anti-Proutian determinations of Stas. If we calculate from Thomsen's new ratio with N = 14 and Cl = 35·5, it gives H = 1·0242; which is most unsatisfactory. In short, the method followed by Thomsen is too indirect and subject to too many possibilities of error to entitle it to much weight in fixing so important a constant as the atomic weight of oxygen. The direct processes, followed by several recent investigators, and giving O = 15·87 to 15·89 are much more trustworthy. Meyer and Seubert (*Ber. d. Chem. Ges.*, xxvii., 2770; see also abstract by Ostwald in *Zeit. Phys. Chem.*, xv., 705), in their criticism of Thomsen's work, have pointed out some of its uncertainties.

In this connection it may be noted that Scott's research upon the composition of water by volume, cited by abstract in the report of last year, has been published in full in the *Philosophical Transactions*, 1893, clxxxiv., 543.

STRONTIUM.

The atomic weight of strontium has been re-determined by Richards (*Proc. Amer. Acad.*, 1894, 369) from analyses of the bromide. The first ratio measured, after a careful preliminary study of materials and methods, was that between silver and strontium bromide. Of this ratio, three sets of determinations were made, all volumetric, but with differences of detail in the process. The weights are as follows, with the ratio $Ag_2 : SrBr_2 : : 100 : x$ in the third column:—

First Series.

	Wt. Ag.	Wt. $SrBr_2$.	Ratio.
	1·30755	1·49962	114·689
	2·10351	2·41225	114·677
	2·23357	2·56153	114·683
	5·36840	6·15663	114·683
Sum	11·01303	12·63003	114·683

Second Series.

	Wt. Ag.	Wt. $SrBr_2$.	Ratio.
	1·30762	1·49962	114·683
	2·10322	2·41225	114·693
	4·57502	5·24727	114·694
	5·36800	6·15663	114·691
Sum	13·35386	15·31577	114·692

Third Series.

	Wt. Ag.	Wt. $SrBr_2$.	Ratio.
	2·5434	2·9172	114·697
	3·3957	3·8946	114·692
	3·9607	4·5426	114·692
	4·5750	5·2473	114·695
Sum	14·4748	16·6017	114·694

From these data we have, if Ag = 107·93, and Br = 79·955 (O = 16), the following results:—

From first series .. .. Sr = 87·644
,, second series .. 87·663
,, third series .. .. 87·668

In two additional series, partly identical with the foregoing, the silver bromide thrown down was collected and weighed. I subjoin the weighings with the ratio $2AgBr : SrBr_2$ in the last column.

First Series.

	2AgBr.	$SrBr_2$.	Ratio.
	2·4415	1·6086	65·886
	2·8561	1·8817	65·884
	6·9337	4·5681	65·883
Sum	12·2313	8·0584	65·8834

Second Series.

	2AgBr.	$SrBr_2$.	Ratio.
	2·27625	1·49962	65·881
	3·66140	2·41225	65·883
	3·88776	2·56153	65·887
	9·34497	6·15663	65·882
Sum	19·17038	12·63003	65·883

From the first series .. Sr = 87·660
" second series.. 87·659

The average of all five series is Sr = 87·659.

(To be continued.)

REPORT OF EXPERIMENTS ON THE CHEMISTRY OF THE CYANIDE PROCESS, AND NOTES ON ITS WORKING.

New Process for Determining Cyanides.

Solubility of Gold in Double Cyanides and in Hydrochloric Acid.

Phenolphthalein as an Indicator in Titrating Potassium Cyanide.*

By G. A. GOYDER, F.C.S.,
Analyst and Assayer to the South Australian School of Mines and Industries.

(Concluded from p. 82).

Another method of working the lixiviation process consists in closing the draw-off pipe and filling the vat with water to the top of the filter bed; the tailings are then filled in and levelled, and the strong solution run on. As the air cannot escape below it bubbles up vigorously through the solution, and appears to form channels in the tailings, which result in irregular percolation afterwards; as the solution sinks, more is added from time to time until the vat is full, when a little of the water is drawn off from below, and the solution is then left standing for about twelve hours. The vigorous bubbling which takes place in the vat also causes the mixture of the strong solution with the residual water in the tailings, and thus increases its bulk. The solution displaced by weak liquor is run off at a quicker rate than above, the rest of the process being the same as there described. Judging the two processes by the appearance of the solutions in the syphon bottles, the former process gave a clearer effluent with quicker changes from one solution to the other, and the solution became colourless at the end with less wash water than the latter. As in the latter process the bulk of solution had already been increased at the beginning the quantity of wash water at the end would have to be reduced, or the volume of solution would become unmanageable, and thus gold would be left in the tailings.

The importance of the above, and especially of a thorough washing of the tailings after treatment by cyanide, is emphasized by an instance described by Caldecott, Johannesburg Chem. and Met. Soc., July 28, 1894, in which he says:—"In the re-treatment of a mass ef residues by the African Gold Recovery Company, from which on the average 70 per cent of the original gold had already been extracted, the extraordinary fact was discovered that their value was no longer 15 dwts., but 9 dwts. only. Explanations as to the reason of this discrepancy were sought for in vain, until, when all the residues had been re-treated, the site they had occupied was sampled, with the result that the top 3 ins. was found to assay 38 dwts. of fine gold per ton, evidently derived from the soluble gold produced by the cyanide solution contained by the residues continuing to act after discharge, and being washed downward by the rain."

It is evident that the above was due to imperfect washing. Whether the cyanogen compounds left in the tailings had already dissolved the gold when these were thrown out or afterwards dissolved it is quite another question; but I believe the former was more nearly the case than the latter, as assumed by Mr. Caldecott.

The time necessary for the lixiviation of a vat of tailings, &c., varies from twenty-four hours, where the gold is very fine and the solutions pass readily through tailings containing little injurious mineral, to a week or even a fortnight, where the gold is coarser, as in concentrates; but in any case I believe that, where possible, it is advantageous to let the solutions run through slowly and regularly, so that they will all pass in the least time necessary for the best payable extraction, reducing the strength of the solution and increasing its bulk where the gold is coarse, rather than to let the solution stand for some time in the ore and then run it off quickly. In the former case the solution is less liable to form channels, and the rate of flow between the coarse and fine interstices is more even than in the latter case. Also where the solution is always moving fresh cyanide is being constantly brought into contact with the small particles of gold, whereas when the solution is standing all the cyanide near a small particle may soon become exhausted, and fresh cyanide is only able to approach to the attack by the very slow process of diffusion. In the experiments I have made on the small scale the slow even flow gave the best extraction in the least time, and no doubt it would be the same on the working scale.

In the following Table the progress of lixiviation of a vat is shown by analyses of samples drawn from the syphon bottle at intervals of an hour, the solutions being allowed to run continuously, the whole process occupying less than twenty-four hours. The percentages of cyanide given were determined with the addition of excess of caustic soda, as above described, and therefore indicate cyanide of potassium plus cyanide of zinc and potassium plus some other double cyanides formed during the extraction, but not including ferrocyanide of potassium, or mercury, or copper-potassium cyanide. The strong solution used contained 0·3 per cent of potassium cyanide and 0·3 per cent of zinc-potassium cyanide, and the weak solution 0·3 of zinc-potassium cyanide. Both solutions contained between 1 dwt. and 2 dwts. of gold per ton remaining from previous operations.

Analyses of Samples of Solution taken from Syphon-Bottle at Intervals of an Hour during the Lixiviation of a Vat of Tailings.

No. of sample.	Appearance in syphon-bottle.	Percentage of cyanide in sample.	Gold per ton of sample.	Solution run to
1..	White	Nil	Nil	Waste water tank.
2..	White	0·002	Trace	
			Dwts. Grs.	
3..	Pale yellow, gradually increasing to full yellow, remaining some time the same tint, gradually decreasing to pale yellow, and becoming very pale.	0·022	0 15	Small zinc boxes.
4..		0·056	1 6	
5..		0·102	8 3	Large zinc boxes.
6..		0·270	9 2	
7..		0·370	—	
8..		0·424	9 18	
9..		0·441	10 13	
10..		0·499	6 12	
11..		0·540	—	
12..		0·550	4 20	
13..		0·500	—	
14..		0·404	2 14	
15..		0·302	—	Small zinc bozes.
16..		0·228	2 6	
17..		0·200	—	
18..		0·180	2 14	
19..		0·150	—	
20..		0·095	2 6	
21..		0·061	1 15	
Left draining..	—	—	—	

It will be noticed that the solutions do not pass as rapidly from one to the other as they should do. This is in consequence of the bottoms of the vats not sloping towards the draw-off pipe, and causing a mixture of the solutions in the vats. Had the vats been properly constructed in this respect I believe the water, at the commencement, could have been run off for another hour or more before the gold appeared, and similarly at the end of the process No. 16 to 18 should have shown 0·3 per cent cyanides, and the percentages then run down rapidly until not more than 0·005 should be contained in the twenty-first hour, while the gold in the same sample should not be more than a trace. It is also very evident that had the first two hours' running been added to the zinc boxes in addition to another hour's running of water at full speed, not included in the table, the same amount would have been left in at the end, and that all the gold indicated from 18 to 21 would thus have been left in the tailings in solution, or the bulk of solution duly increased.

The next Table, which gives the result of a laboratory experiment, is not strictly comparable to the last one, as the ore was dry at the start and had not had the coarse gold removed by the battery. The bottom of the apparatus, however, sloped properly to the draw-off pipe, and it will be noticed how rapidly the strength of the solution, both in cyanide and gold, decreases after No. 15, when the wash-water began to appear, and on the large scale I believe it would decrease even more rapidly than this. The percentage of cyanide in the solutions was determined by the ordinary process, without the addition of caustic alkali. It will be noticed that the solutions contain rather more gold after standing than before, but much of the gold in this stone was much coarser than would obtain in an ordinary tailings, and a larger excess of cyanide was present than would be the case on the working scale; 3000 c.c. of cyanide solution, 0·2 per cent, was gradually poured on the ore, and was collected in lots of 200 c.c. for analysis.

Analysis of Solutions running from Experimental Percolator during the Lixiviation of a Rich Sample containing Coarse Gold.

200 c.c.	Per cent of cyanide in sample.	Gold per ton in sample.			Remarks.
		Ozs.	Dwts.	Grs.	
1.. ..	0·044	4	9	0	
2.. ..	0·103	5	16	0	
3.. ..	0·147	4	10	0	
4.. ..	0·165	3	1	0	Stopped and left standing 17 hours.
5.. ..	0·158	3	11	0	
6.. ..	0·180	2	6	0	Stopped for 46 hours.
7.. ..	0·154	2	20	0	
8.. ..	0·172	2	12	0	
9.. ..	0·172	1	8	0	
10.. ..	0·172	0	19	0	Stopped for 18 hours, and wash-water added.
11.. ..	0·145	0	12	0	
12.. ..	0·154	0	6	12	
13.. ..	0·176	0	4	21	
14.. ..	0·165	0	4	21	
15.. ..	0·091	0	3	20	Wash-water begins to show.
16.. ..	0·015	0	0	18	Cyanide solution nearly all gone.
17.. ..	0·005		trace		

Some experiments were made at Mount Torrens to determine whether by allowing each lot of solution added to the tailings to drain away before adding more solution, and so causing the air to penetrate the tailings intermittently with the solution, a more perfect extraction could be attained. As, however, the results were no better than by the usual method, and as unnecessary aëration promotes loss of cyanide, it appears better to add the solutions until the last wash water has been added as soon as the previous lot has sunk to the surface of the tailings.

A sample of concentrates, mostly pyrites, received here for testing as to its suitability for treatment by the cyanide process, was found by a preliminary washing to contain so much ferrous sulphate as to decompose cyanide of potassium at the rate of about 150 lbs. per ton of concentrates. After washing, however, 67 per cent of its gold contents were extracted without undue consumption of cyanide. In last year's report I alluded to the Eureka ore as requiring too much cyanide to be profitably treated by that process. The basic salts in this ore are not readily removed by washing; but when the ore is passed through the battery these salts are so effectually removed as to make the tailings readily amenable to treatment by cyanide. A sample analysed by me contained about ½ per cent of copper. W. R. Feldtmann (*loc. cit.*) recommends that where tailings require a preliminary wash before treatment by cyanide, that the washing should be done in a separate vat reserved for that process only, as "when a water wash charged with acid out of the ore comes in contact with residual quantities of cyanide solution lying in the bottom and adhering to the sides of the tank, a certain quantity of hydrocyanic acid gas is liberated, which, diffusing through the whole tank, is capable of dissolving a not inconsiderable amount of gold from the ore; such dissolved gold is not precipitated even if passed through zinc, and is consequently run to waste with the water wash." In this explanation Mr. Feldtmann appears to assume that the solvent action of hydrocyanic acid on gold is at least equal to that of cyanide of potassium. As I have seen no records of experiments on this point I have just made one, placing a gold leaf in a bottle and adding 50 c.c. of 1 per cent cyanide of potassium, to which an equivalent of hydrochloric acid had just been added to set free the hydrocyanic acid: after being left in the bottom for four days, with occasional violent shaking, the solution was filtered off from the undissolved gold, and the gold dissolved was found to amount to 65 per cent of the whole taken. The solvent action of hydrocyanic acid on gold in the presence of air is therefore decided, but very slow. A solution of cyanide of potassium of 0·1 per cent would have dissolved the whole of the gold leaf under similar circumstances in about five minutes.

Judging, however, from the complete removal of soluble salts from the Eureka ore in passing through the battery, it appears to me that with a sample of tailings containing deleterious soluble salts, and not requiring to go through the battery, these salts could be most effectually removed by passing the tailings over a shaking table, using plenty of water.

The large quantity of cyanide of potassium decomposed by ferrous and other soluble metallic salts points to the advisability of transferring the tailings, and especially those containing pyrites, from the pits to the vats with as little exposure to damp air as possible, and also of testing the water running from the vats before the addition of cyanide to ascertain whether a preliminary wash is required.

In order to ascertain whether the gold left in the tailings after treatment by cyanide could be extracted by further treatment, I procured from Mr. L. W. Grayson a sample from the tailings heap at Mount Torrens, and treated a portion of it with excess of ¼ per cent cyanide of potassium by continuous percolation for forty-eight hours, thoroughly washing out the cyanide at the end. The tailings before treatment contained gold at the rate of 1 dwt. 13 grs. per ton, of which 8 grs. were extracted by the above treatment. The same sample was again treated in a similar manner by fresh solution, but only yielded ⅛ gr. per ton. The same sample was then treated with a large excess of strong bromine water during three days, percolating during the day and stopping with the percolator full during the night. During this treatment the small quantity of pyrites present was oxidised, but no gold was dissolved.

The sample was then removed from the percolator, dried, and separated by sieves into three grades, which were assayed separately with the following result—the number of the sieves represent holes per linear inch:—Two per cent, retained by 30-sieve, assayed 8 dwts. 3 grs. of gold per ton; 29 per cent, retained by 60-sieve, assayed 2 dwts. 7 grs. of gold per ton; 69 per cent, which passed 60-sieve, assayed 14 grs. of gold per ton, from which it was calculated that the gold would be divided as follows in a ton of the tailings:—Three grains of gold would be contained in 45 lbs. of coarse tailings; 17 grs. of gold would be contained in 650 lbs. of medium tailings; 11 grs. of gold would be contained in 1545 lbs. of fine tailings.

Another sample treated in a similar manner yielded:—20·6 per cent, retained by 40-sieve, assayed 3 dwts. 7 grs. of gold per ton; 12·0 per cent, retained by 60-sieve, assayed 2 dwts. of gold per ton; 67·4 per cent, that passed 60-sieve, assayed 1 dwt. 4 grs. of gold per ton. Therefore, 16 grs. of gold would be contained in 460 lbs, of coarse tailings; 5 grs. of gold would be contained in 270 lbs. of medium tailings; 18 grs. of gold would be contained in 1510 lbs. of fine tailings.

Another sample of tailings which had been treated by cyanide contained 3 dwts. of gold per ton, and yielded 1 dwt. to further treatment as above by cyanide, and the gold remaining was equally distributed in the coarser and finer portions.

It would therefore appear that this residual gold cannot be extracted by solvents without further comminution of the tailings, and must therefore be surrounded by matrix impermeable to the solutions. It is further evident that in the above-cited cases the tailings could hardly pay the cost of concentration, re-crushing, &c., necessary to extract some of the balance of the gold.

During my stay at Mount Torrens in April, I inferred from the method in which the cyanide process worked that the double cyanide salts present in the sump liquors must have a considerable solvent action on gold, and found on testing some of these sump liquors that they dissolved gold leaf at about a third of the rate of alkaline cyanide. After my return, therefore, I prepared some of these double cyanides and purified them by crystallisation, several times repeated, and found that zinc potassium cyanide dissolved gold in the presence of oxygen with the production of gold potassium cyanide and oxide of zinc; part of the cyanide also appeared to be transformed into aurocyanide of potassium and auricyanide of zinc, zincate of potash being also produced thus:—

$$K_2ZnCy_4+Au_2+O=2KAuCy_2+ZnO, \text{ and}$$

$$4K_2ZnCy_4+4Au+3O_2= \\ =Zn(AuCy_4)_2+2KAuCy_4+3Zn(OK)_2.$$

The cyanide of copper and potassium reacted in a similar manner, but somewhat more slowly.

The double cyanide of mercury and potassium does not appear to dissolve gold, even after four months' contact, with occasional shaking. This experiment, however, is not yet finished.

I have not yet tested the double cyanide of calcium and potassium, which may be present in sump liquors from double decomposition, but probably it would be a better solvent for gold than the zinc double salt.

According to W. R. Feldtmann (*Engineer and Mining Journal*, lviii., 1894, 218, 219) the African Gold Recovery Company have made sone experiments recently, showing that zinc potassium cyanide has a solvent action on gold in its ores and in the absence of any free potassium cyanide.

I have not yet had time to investigate the nature of the double salts formed in the lixiviation process apart from those formed in the zinc boxes, but believe there must be some double salt (or salts) formed which is more active as a solvent for gold than the double zinc salt. Possibly it may be the double iron salt, K_2FeCy_4, but this is quickly converted by excess of cyanide of potassium into ferrocyanide of potassium, which I find takes months to dissolve gold leaf. I have not had time to determine the reactions involved.

To the solvent action of these double salts on gold, especially on ores containing copper or other "refractory" minerals, the success of the cyanide process is without doubt to a large extent to be attributed.

NOTICES OF BOOKS.

The Chemistry of Urine. A Practical Guide to the Analytical Examination of Diabetic, Albuminous, and Gouty Urine. By Alfred H. Allen, F.I.C., F.C.S., Past President of the Society of Public Analysts, &c. 8vo., pp. 212. London: J. and A. Churchill. 1895.

The author of this manual tells us that he has been led to take up thoroughly the chemical examination of urine, with especial reference to the requirements of physicians called on to act as referees for Life Assurance Companies as well as in questions of diagnosis and prognosis. Hence Mr. Allen has given special attention to the examination of diabetic, albuminiferous, and gouty urines. It has not been his object to produce a complete manual of urinary analysis.

The various methods for the scrutiny of urines are critically examined, and the conditions of their trustworthiness or fallibility are carefully expounded. Hence the book will be of sterling value not merely to physicians, but also to analysts, especially such as have not made this department of chemistry a leading study.

The Consistence-Meter, German Patent, No. 81,265. (Der Consistenz-Messer, D.R.P. 81,265). Berlin: Bernhard Paul.

This pamphlet is in substance the very voluminous specification of a German patent. The author, Dr. Weiss, has devised an instrument by which the amount of solids contained in an extract, solution, &c., is estimated by the sinking of a suspended disc. The procedure is applied to fatty oils, solutions of gums, sugars, milks, beers, to the determination of starch in grain, in potatoes, seedcakes, &c.

The general question arises, whether patents for any analytical or other scientific appliance are not objectionable on the same principle as is a patent for an analytical procedure.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 4, July 22, 1895.

Osmotic Phenomena produced between Ether and Ethylic Alcohol, through different Diaphragms.—F. M. Raoult.—The author's experiments prove that the osmose between two given liquids may not merely vary greatly in energy, but even change its direction with the nature of the diaphragm, and that the osmotic movement of substances through the diaphragm may be absolutely independent of their molecular weight and of their function as dissolved bodies or as solvents.

Action of Phenyl Isocyanate upon certain Acids and Ethers.—A. Haller.—Not suitable for useful abstraction.

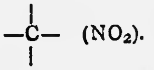
On Crystalline Anhydrous Manganese Hydrate.—A. Bourlot.—This paper will be inserted in full.

Certain Properties of Compounds of Ferrous Chloride and Nitric Oxide.—V. Thomas.—The author seeks to ascertain whether the compounds which he has recently obtained (*Comptes Rendus*, Feb. 28th and July 8th, 1895) are or are not dissociable. He concludes from his experiments that none of the three compounds described has a tension of dissociation appreciable at the ordinary temperature. There is a very decided difference between the compounds obtained by M. Gay in the state of solution and those which the author has obtained by the dry way.

On some Alkaline Phosphides.—C. Hugot.—The two phosphides P_5K and P_3K, the preparation of which he describes, are decomposed by moist air with disengagement of hydrogen phosphide. If an excess of ammonium is caused to act upon red phosphorus we obtain new compounds which the author is studying.

Specific Heats of Superfused Formic and Acetic Acids. Modifications to be introduced into Regnault's Thermo-calorimeter for the Determination of the Specific Heats of a great number of Superfused Liquids.—MM. Massol and Guillot.—The specific heats in the solid state are much higher than the specific heats in the liquid state. The specific heat in the liquid state decreases with the temperature. In the state of superfusion the specific heat augments slightly.

Synthetic Formation of Mixed Alcohols.—Louis Henry.—The reactional capacity of methanal with nitromethane, nitro-ethane, and nitro-isopropane corresponds to the number of hydrogen atoms enclosed in the carbonitic system.



$$-\overset{|}{\underset{|}{C}}-\quad (NO_2).$$

Oxidation of Inactive Campholenic Acid.—A. Behal. —Not suitable for abridgment.

Constitution of Vegetable Albumenoid Substances. —E. Fleurent.—The failure of the proportion—

$$\frac{\text{N determined}}{\text{N calculated}} = 1$$

is due to the presence in gluten, caseine, and vegetable fibrine of a glutamine group, and in legumine and vegetable albumen of an asparagine group.

No. 5, July 29, 1895.

Action of Aniline upon Mercurous Iodide. — Maurice François. — The decomposition of mercurous iodide by aniline is limited, and it is the same with the combination of mercuric iodide and mercury in presence of aniline. The author finds that when a state of equilibrium is reached the liquid always contains, at the boiling-point of aniline (182°), 26·35 grms. mercuric iodide in 100 grms. of the mixture. The action of aniline upon mercurous iodide is comparable to the action of water upon bismuth nitrate, mercuric sulphate, &c., studied by M. Ditte, and follows analogous laws.

Action of Hyponitric Anhydride upon Campholenic Acid.—MM. A. Béhal and Blaise.—If we fix a mol. of NO_2, and treat the blue liquid with a saturated solution of potassium bicarbonate, there remains a blue insoluble oil, which soon solidifies. When re-crystallised from alcohol at 80° it forms slender blue laminæ, fusible at 134·5, having the composition $C_{10}H_{15}NO_3$. It is neutral, does not decompose alkaline bicarbonates, and may be obtained in two modifications, which may be named ceruleonitrosocampholenolide and leuconitrosocampholenolide.

The Condensation - Products of Isovaleric Aldehyd. — L. Kohn. — The author has obtained two products; the one, boiling at 82° under a pressure of 15 m.m., seems identical with that studied by Kekulé, Fittig, Beilstein, and others, and probably with the product obtained by Barbier and Bouveault. The second product is an oil of feeble odour, colourless, boiling at 140° under a pressure of 18 m.m. It seems to be a polymer of valerol.

The Determination of Boric Acid.—MM. H. Jay and Dupasquier.—This paper will be inserted in full.

Revue Universelle des Mines et de la Metallurgie.
Vol. xxx., No. 2.

This issue contains no chemical matter.

MISCELLANEOUS.

Responsibilities of Manufacturers in Germany.— The following remarkable decisions against employers have been lately given by the "Reichs versicherungs Amt":—*a*. The death of a workman in consequence of drinking, at the Works, out of a bottle containing hydrochloric acid, in mistake for a bottle of "schnaps" which the deceased had brought with him. *b*. Malicious poisoning by a fellow-workman, on the pretext that the quarrel was due to a disagreement over work. *c*. Injuries from the explosion of a dynamite cartridge which workmen on strike had left on the premises with criminal intent. *d*. A workman was overwhelmed with stones, &c., in a quarry; a fellow-workman, suffering from palpitation, was so excited that he died. *e*. In order to cure an injury to the fingers, received whilst at work, a labourer was sent by his employers to a medical institute at Hamburg. Whilst there (in autumn, 1892) he died of cholera, and his death was decided to be a working disaster. (Which of these decisions is the most signally inequitable might be the subject of a prolonged discussion.) – *Chemiker Zeitung*.

On Periodical Fluctuations of the Intensity of the Earth's Gravity, and their Influence on Determinations of Atomic Weights.—Dr. G. Paul Drossbach.— If a metallic cone with a very obtuse optical angle is brought in contact with a mercurial horizon, the slightest fluctuations of the level of this cone must present the most different resistances conceivable to a quantity current. For the experiment the cone is suspended to a metal spring. The resistance varies from morning to evening, all accessory causes being of course taken into account. The difference of gravitation was compensated by the addition of weights and thus directly determined. The difference between morning and evening seems to be 0·008 grm. per 100 grms. This indicates a speed of the movement of gravity of about 380 to 400 m.m. The difference between midnight and noon seems to be rather greater, so that the maximum effect of gravitation falls at midnight and morning.—*Chemiker Zeitung*.

NOTICE.

The STUDENTS' NUMBER of the Chemical News *will be published on Friday, September 6th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.*

Advertisements for this Number should reach the Office not later than Wednesday, th4 Sept.

THE CHEMICAL NEWS.

VOL. LXXII., No. 1866.

THE SPECTRUM OF RAMSAY'S COMPOUND OF ARGON AND CARBON.

By WILLIAM CROOKES, F.R.S., &c.

IN the CHEMICAL NEWS for the 2nd of August last (vol. lxxii., p. 51) Professor Ramsay announced the probable existence of a compound of argon and carbon formed by an electric arc between purified carbon poles in an atmosphere of argon. Professor Ramsay kindly filled a quarz-ended tube for me with the resulting gas at the requisite degree of exhaustion for the greatest luminosity, and I have taken several observations on its spectrum, both by the eye and photographically.

The eye observations show an extremely luminous spectrum, in which many of the stronger lines of argon are visible. Measurements were taken of the following argon lines:—

7646
7506
7058
6965·6
6664
6407
6173
6045
6038
5909
5887
5834
5803
5771
5651
5610
5557
5496·5
5185·8
5165
4879
4509·5
4335
4272
4259·5
4201
4159·5

On comparing these with the extended table of the argon spectrum given in the CHEMICAL NEWS for August 9th, it will be seen that they include all the strongest lines in the visible spectrum. Others, less intense, would probably have been seen had not the luminosity of the continuous spectrum interfered with vision.

Examination of the photographs show that in the ultra-violet portion of the spectrum there are also many argon lines, but a little above wave-length 3400 the strong lines due to water-vapour interfere too much to allow the argon lines to be detected.

The higher portions of the visible spectrum show finely channelled groups. These are very prominent in the photographs, and on superposing them on photographs of benzene vapour, carbonic anhydride, and cyanogen, taken under identical conditions, it is seen that the channelled bands are due to a carbon compound, the argon-carbon bands being identical with some of those of cyanogen and carbonic anhydride, and not so strong.

I have looked in vain for lines which are not in the argon, carbon, or water-vapour spectra, and have not found any.

The spectrum of water-vapour is due to moisture, the gas not having been perfectly dried before it was sealed in the tube.

The argon lines are probably caused by excess of argon mixed with the argon-carbon compound, the mode of formation making it very unlikely that all the argon had united with carbon.

Professor Ramsay informed me that the nitrogen had all been removed from the argon before it was submitted to the action of the arc, and special precautions were also taken to remove occluded gases from the carbon-poles.

The coincidence of some of the bands of the new compound with those of cyanogen must not be used as an argument in favour of the theory that argon is a condensed form of nitrogen. Most volatile compounds of carbon have very similar spectra. If photographs of the spectra of carbonic anhydride, carbonic oxide, benzine-vapour, cyanogen, &c., are superposed, there will not only be seen a general resemblance between them, but in many of the systems of fluted bands there is absolute identity. All that can be said, therefore, is that the compound of argon and carbon gives a similar spectrum to that of most carbon compounds.

I have looked in vain for any line of helium in this spectrum.

London, August 14, 1895.

THE BLUE SPECTRUM OF ARGON.

By Prof. H. KAYSER.

IN the following Table I give a preliminary list of the wave-lengths of the lines of the blue argon-spectrum between $\lambda = 340\ \mu\mu$ and $\lambda = 520\ \mu\mu$.

The gas was prepared from atmospheric air, first by copper and magnesium, then by sparking in the presence of caustic potash and absorbing the oxygen by pyrogallic acid and caustic potash. Finally, the gas was dried by phosphorus pentoxide. At different times small quantities of argon were thus prepared, and many Geissler tubes filled at a pressure of 2·2 m.m., which seemed to give the best results. With a Leyden jar and air break a beautiful blue light is produced. The spectrum was photographed with a large Rowland concave grating of 21 feet radius. The different tubes all gave the same lines, only one tube showed the hydrogen lines, and in another appeared the strongest lines of the red argon spectrum. I have photographed also the red spectrum, which appears without a Leyden jar, but have not yet finished the measurement and calculation of the plates. The two spectra have no lines in common, as far as I see.

For the calculation of the wave-lengths in every case the spark spectrum of iron was photographed at the same time on the plates, so that no shifting of the two spectra could occur. For the wave-lengths of the iron lines Rowland's standards were taken.

The numbers in the Table are means of 3 to 6 independent measures; the stronger lines may have an error amounting to 0·001 $\mu\mu$, but the weaker ones are less accurate, and it is not impossible that in a few cases there may be an error of 0·01 $\mu\mu$. 10 signifies the greatest intensity, 1 the weakest. The lines of the blue argon spectrum do not appear among the Frauenhofer lines, as appears from a comparison with Rowland's publications on the lines of the solar spectrum.

I shall soon add the red, yellow, and the remaining ultra-violet part of the blue spectrum, and also the red one; then I shall also discuss these spectra for series. I wish only to state yet, that the red argon line at 706·7 $\mu\mu$ is not coincident with the red helium line at 706·5 $\mu\mu$, but has a greater wave-length.

3454·291	2	3521·428	2
3464·387	2	3522·098	1
3466·333	2	3535·517	3
3476·921	5	3545·778	5
3478·385	1	3546·016	5
3480·643	5	3548·705	2
3491·019	1	3559·707	8
3491·420	5	3561·218	7
3491·705	7	3565·223	2
3499·812	3	3576·810	8
3502·342	2	3581·804	4
3503·715	2	3582·550	7
3509·475	3	3588·634	9
3509·962	3	3592·231	1
3511·284	8	3606·072	2
3511·790	1	3622·362	2
3514·354	4	3638·025	7
3514·561	4	3640·024	2
3517·942	1	3651·132	1
3520·179	3	3655·465	3

3656·264	1	4089·041	1
3660·636	1	4104·102	7
3669 632	1	4112·915	1
3678·476	2	4131·919	4
3680·075	1	4146·761	1
3692·736	1	4156·293	2
3712·963	1	4178·477	1
3716 667	1	4179·478	1
3717·316	1	4183·109	2
3718 393	3	4199·226	1
3720 609	1	4202·115	2
3724·563	1	4203·592	1
3729·464	9	4218·867	3
3738·084	3	4222·848	3
3750·294	1	4227·142	2
3753·768	1	4228·301	5
3756·529	1	4229·059	1
3763·718	3	4229·874	1
3765·461	5	4237·397	3
3766·317	2	4266·385	6
3770·721	2	4275·330	1
3776·885	1	4277·720	6
3781·022	6	4283·084	3
3786·558	2	4298·215	1
3795·512	3	4300·817	2
3799·615	2	4309·317	2
3800·429	1	4331·359	6
3803·383	2	4332·205	3
3808·754	1	4333·701	2
3809 645	3	4335·471	1
3825·831	1	4337·258	1
3826·983	3	4343·912	2
3830·603	1	4345·330	1
3841·706	1	4348·231	10
3844·905	1	4352·374	4
3845·536	1	4362·240	2
3850·721	8	4367·963	1
3858·467	2	4370·921	4
3868·700	6	4371·504	4
3872·345	2	4375·266	1
3874·288	1	4376·129	3
3875·413	3	4379·832	6
3880·432	1	4383·900	2
3891·547	2	4400·269	3
3892·118	4	4401·165	5
3900·750	1	4408·102	1
3907·896	1	4421·102	1
3911·678	1	4426·170	9
3914·918	3	4430·365	6
3925·897	3	4431·176	4
3928·750	7	4434·010	2
3931·348	1	4439·541	1
3932·705	4	4443·545	1
3937·208	1	4449·128	2
3944·412	4	4460·683	2
3946·275	3	4475·035	2
3952·868	1	4482·000	5
3960·620	2	4498·874	1
3968·499	3	4503·099	1
3974·662	1	4545·231	5
3979 517	3	4579·531	5
3992·208	2	4589·087	5
4013·997	6	4609 750	6
4023·730	1	4658·070	4
4034·009	2	4727·032	4
4035 630	2	4736·069	5
4038·968	2	4765·030	3
4043·047	4	4806·185	6
4053·118	1	4847·965	3
4072·158	7	4897·997	4
4072·587	3	4965·234	2
4076·869	2	5009·615	2
4077·207	2	5017·421	1
4079·732	2	5062·258	2
4080·850	1	5145·659	2
4082·553	1		

Bonn, July 12, 1895.

ON THE PRODUCTION OF CITRIC ACID FROM CANE-SUGAR.

(Second Note).

By Dr. T. L. PHIPSON.

When I published my recent note on this subject I should have remarked that Prof. Maumené (*Comptes Rendus*, April 8, 1895) had already obtained two new organic acids by the action of permanganic acid on cane-sugar; and that Liebig formerly announced that he had obtained tartaric acid by the action of dilute nitric acid on sugar.

I have found that in the grape, the apple, &c., these acids disappear as the sugar is formed, from the outside to the inside of the fruit, and that the remaining acid is concentrated around the seed, probably acting as an antiseptic until germination ensues. It is thus evident that organic acids are formed in fruits before the sugar is formed, and that the sugar may possibly be derived from them. Nevertheless, the ease with which sugar is converted into carbonic acid, formic acid, oxalic acid, &c., and its original production from the starch of the seed during germination, points to the possibility of all other organic acids devoid of nitrogen being obtainable from sugar.

In treating cane-sugar in the cold with permanganic acid as described in my first note, I obtained an acid having some resemblance to citric acid, but no sufficient quantity was obtained to prove its real nature, and I have since been unable to repeat this experiment, but hope to do so shortly. I found, however, that other acids are liable to be formed at the same time, according to the degree to which oxidation is allowed to proceed.

Some chemists who have repeated my first experiment have only succeeded in obtaining sulphate of lime. Probably they used too much sulphuric acid, and did not separate the organic acid by alcohol as I did.

The Casa Mia Laboratory, Putney,
London, August 20, 1895.

SEPARATION OF GOLD AND SILVER FROM IRON AND STEEL.

By H. N. WARREN, Research Analyst.

To make an accurate and complete analysis of either iron or steel, as is well known, frequently requires a considerable quantity of the sample under examination to become dissolved or otherwise acted upon, in order to ascertain the various constituents present, which are otherwise rendered latent by the large excess of iron associating them. But cases are few and far between where 4 lbs. in weight have to be operated upon, as was the case last week at the Research Laboratory, when an extraordinary examination was required in order to ascertain the relative amounts of both gold and silver present. For examination and estimation of silver 4 lbs. in weight of each sample were selected, the product being bar iron of one inch circumference; each bar was attached to the positive of a battery of 3 volts 40 ampères, whilst a carbon electrode furnished the negative, dilute vitriol being employed as the solvent. Dissolution was completed in forty-eight hours, save a thin wire of iron, which was allowed to remain in order to ensure retention of the silver present in the carboniferous residue.

The residue was next dried and intimately mixed with an excess of chemically pure litharge and reduced in the usual way. The silver separated by cupellation, and gold by parting.

Of the four samples thus treated, the silver, being estimated as percentage of the carboniferous residue, amounted to as follows:—Iron of Swedish origin, 0·8; silver from Shortridge and Howel, 0·055; Low Moor iron, 0·100; Dannemora, 0·064; in each case traces of gold were obtained by parting.

Bars of steel similarly treated yielded percentages approximating 0 078, 0·043, 0·098, 0·032.

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

GRADATION IN PRESSURES.

By Dr. L. C. LEVOIR.

The principle of gradation in pressures, utilised in so prolific a manner by Cailletet, in condensing such gases as oxygen and hydrogen, is useful in organic chemistry for saving the life of sealed tubes and valuable preparations.

"Krakatooing" was the term which my students used when in the Bomb Room sealed tubes in the apparatus of Carius, &c., fell to ruin. Bursting can easily be prevented by heating the sealed tube by means of a coil glowing by electricity. The conductor passes through isolated plugs hermetically sealed in inward conical tubes. By a hydraulic pump the pressure outside of the sealed tube is increased. I used a series of ends of boiler tubes, and they worked as a vault or arch to charge or burden the breakable tube outside. In this way, in five successive small boilers, and the coiled tube in a vessel of earthenware without bottom, rolled in vulcanised indiarubber cloth, I have saved the lives of many tubes. I heated water saturated at 0° with hydrochloric acid to 250° without loss.

Rysvick, near The Hague,
August 10, 1895.

A REFORM IN CHEMICAL, PHYSICAL, AND TECHNICAL CALCULATIONS.

By C. J. HANSSEN, C.E.

(Continued from p. 9).

Evaporation of Water (Steam).

If water is heated in a hermetically closed vessel, the steam produced is under the condition "constant volume." In the working of steam boilers, this is only the case while a boiler is started or "fired up," or during interruptions of the working; in boilers in regular work the steam flows out as fast as it is produced, and the quantity of water in the boiler and the quantity of heat stored up in the water remain unaltered, although new water is fed into the boiler to make up for the water passing off as steam.

The quantity of heat required to evaporate 1 kgr. of water, and which passes away with that 1 kgr. of steam, has only passed from the fire *through* the water stored up in the boiler; and to find the quantity of heat theoretically required to produce 1 kgr. of steam, of any desired density, we have only to ascertain how much heat that 1 kgr. of steam is able to contain. The specific heat of water at various temperatures has no influence in the question, and has only to be considered if we were to ascertain the exact quantity of heat required to "fire up" a boiler.

In a boiler in regular working the condition is "*evaporation at constant pressure*," just the same as evaporation in an open vessel would be if the atmosphere of our globe had the pressure or density existing in the steam boiler; and the temperature of saturated steam in a boiler is equal to the temperature at which water would boil in an open vessel, in an atmosphere equal in density to that in the boiler.

Although steam, for practical purposes, is generated by the evaporation of water, it is useful for the investigation of its properties to consider the production of steam by combination of hydrogen and oxygen, which enables us, in a very simple way and more accurate than by experiment, to find volume, weight, pressure, and other properties of steam, due to any temperature, &c.

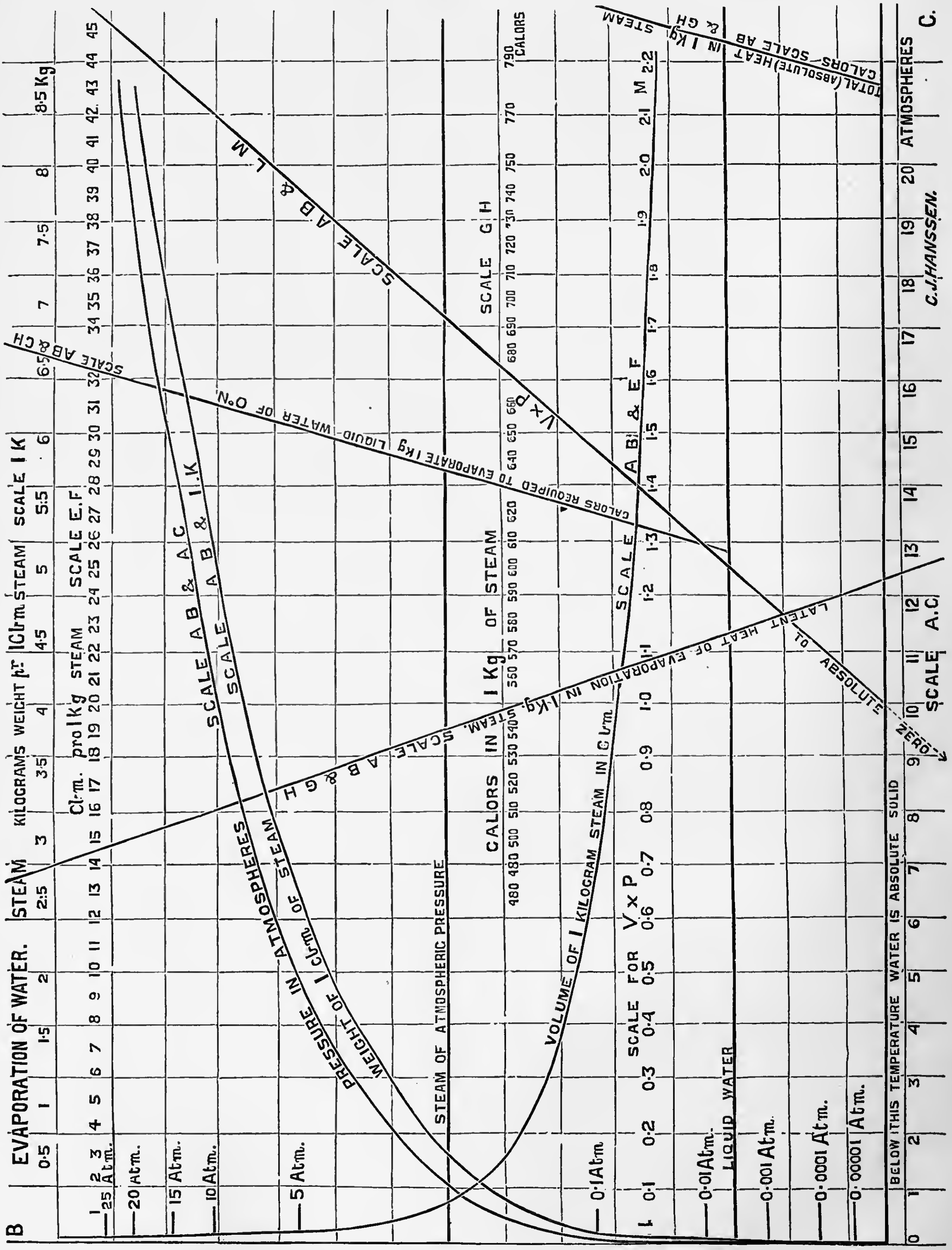
In the former chapters it is shown that 1 cbm. steam of atmospheric density and 273° N. absolute temperature (0° N.), formed of combined H and O, must weigh 45/56 kg., that 1 kg. of similar steam is = 56/45 cbm. in volume, and that heated to 373° N. absolute (+100° N.), the proper temperature of saturated steam of atmospheric pressure, the volume of 1 kg. of steam will be increased to—

$$\frac{56 \times 373^{\circ}}{45 \times 273^{\circ}} = \frac{2984}{1755} \text{ cbm.} = 1·7002849 \text{ cbm.},$$

and the weight of 1 cbm. of such steam will consequently be—

Table of Saturated Steam.

Pressure. Atmospheres.	Temperature. °N.	Weight of 1 cbm. in kg.	Volume of 1 kg. in cbm.	Heat required to evaporate 1 kg. liquid water of 0° N. Cal.	V × P.	Heat required to produce 1 cbm. of steam from water of 0° N. Calor.
0·0042	±0·000	0·003375	296·296	606·700	1·24444	2·04658
0·010	+10·000	0·007750	129·003	610·700	1·29003	4·80377
0 050	+33·960	0·035734	27·985	616·888	1·39925	22·04264
0·100	+46·000	0·06877	14·541	620·500	1·4541	42 67230
0·200	+59·997	0·13176	7·590	624·699	1·5180	82·30747
0·300	+68·328	0·19281	5·186	627·189	1·5558	120·93928
0·400	+76.327	0·25120	3·981	629·598	1·5924	158·15118
0·500	+81·940	0·30903	3·236	631·282	1·6180	185·08179
0·600	+86·592	0·36604	2·732	632·678	1·6392	231·58120
0·700	+90·591	0·42235	2·368	633·877	1·6567	267 68231
0·800	+94·091	0·47808	2·092	634·927	1·6736	303·51042
0·900	+97·201	0·53333	1·875	635·860	1·6875	339·12458
1·000	+100·000	0·588137	1·7002849	636·700	1·7002849	374·46665
2·000	+120·996	1·11359	0.898	642·999	1·7960	716·03180
3·000	+134·993	1·61308	0·620	647·198	1·8597	1043·84457
4·000	+145·491	2·09682	0·477	650·347	1·9080	1363·45964
5·000	+153·889	2·56946	0·389	652·867	1·9460	1678·30680
6·000	+160·888	3·03362	0·330	654·966	1·9776	1987·10798
7·000	+166·886	3·49096	0·286	656·766	2·0048	2293·08974
8·000	+172·135	3·94262	0·254	658·340	2·0312	2595·90064
9·000	+176·801	4·38944	0·228	659·740	2·0502	2896·09214
10·000	+181·000	4·83204	0·207	661·000	2·0696	3193·4334
15·000	+199·033	6·97096	0·143	666·410	2·1510	4646·8807
20·000	+212·500	9·03708	0·111	670·450	2·2120	6059·1322


EVAPORATION OF WATER.
STEAM KILOGRAMS WEIGHT pr. 1 Cb.m. STEAM
SCALE I K
0.5 1 1.5 2 2.5 3 3.5 4 4.5 5 5.5 6 6.5 7 7.5 8 8.5 Kg
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 34 35 36 37 38 39 40 41 42 43 44 45
Cb.m. pro 1 kg STEAM
SCALE E.F
25 Atm.
20 Atm.
15 Atm.
10 Atm.
5 Atm.
0·1 Atm.
0·01 Atm.
0·001 Atm.
0·0001 Atm.
0·00001 Atm.
LIQUID WATER
STEAM OF ATMOSPHERIC PRESSURE
CALORS IN 1 Kg OF STEAM
480 480 500 510 520 530 540 560 570 580 590 600 610 620 640 650 660 680 690 700 710 720 730 740 750 770 790 CALORS
SCALE G H
SCALE FOR V x P
0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 M
SCALE A B & E F
V x P
SCALE A B & L M
SCALE AB & GH
CALORS REQUIRED TO EVAPORATE 1 Kg LIQUID WATER OF 0°N.
LATENT HEAT OF EVAPORATION IN 1 Kg. STEAM. SCALE A B & G H
TO ABSOLUTE ZERO
TOTAL (ABSOLUTE) HEAT IN 1 Kg STEAM CALORS – SCALE AB & GH
VOLUME OF 1 KILOGRAM STEAM IN Cb.m.
PRESSURE IN ATMOSPHERES
WEIGHT OF 1 Cb.m OF STEAM
SCALE A B & A C
SCALE A B & I.K
BELOW THIS TEMPERATURE WATER IS ABSOLUTE SOLID
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 ATMOSPHERES
SCALE A.C
C.J.HANSSEN.
B
A
C.
+240° +220° +200 +180° +160° +140° +120° +100° +80° +60° +40° +20° ±0° −20° −40° −60°

$$= \frac{1755}{2984} \text{ kg.} = 0{\cdot}5881367 \text{ kg.}$$

From these data, other properties of steam may be found by the following simple equations, where in all cases—

V denotes the volume of 1 kg. steam of any pressure in cbm.
W denotes the weight of 1 cbm. steam in kilogrms.
P denotes the pressure of steam in atmospheres absolute.
T denotes the absolute temperature of steam in °N.

1. $V \times W = 1$
2. $\frac{8\,T}{1755\,P} = V$ (cbm.)
3. $\frac{1755\,P}{8\,T} = W$ (kg.)
4. $\frac{8\,W}{1755} = P$ (cbm.)
5. $\frac{1755\,P}{8} = T$ (°N.)
6. $\frac{8\,T}{1755} = P \times V$ (coeff.)
7. $\frac{1}{W} = V$ (cbm.)
8. $\frac{1}{V} = W$ (kg.)

The accompanying Table gives, as a sample, a few of the results obtained by these formulæ, which also, in diminished scale, are shown in the diagram, and which agree very closely with M. Regnault's experiments.

(To be continued.)

3, Valdemarsgade, Copenhagen, V.
July 22, 1895.

ON THE

DIRECT SPECTRUM ANALYSIS OF MINERALS AND OF SOME FUSED SALTS.

By A. de GRAMONT.

I solicit the Academy for permission to summarise the general results not only of the papers which I have already had the honour of presenting, but also of researches which are now in the course of execution.

A great number of minerals are sufficiently conductive or capable of volatilisation to give passage to the electric spark between two of their fragments connected respectively to the poles of an induction-coil with a condenser intercalated. Under these conditions the spark produced behaves in the spectroscope like that of a metallic alloy, but giving along with the rays of the metals contained in the mineral those of the non-metals with which they are combined.

On suppressing the condenser the spectra of the non-metals disappear, and those of the metals are reduced to their most brilliant rays, showing out in general upon the luminous ground produced by the incandescence of the fragments.

A certain number of melted salts, the study of which I have undertaken, especially the haloid salts, have given the same results, which may be generalised thus:—

The condensed spark, playing on the surface of a compound, dissociates it, giving a line-spectrum generally very bright, where each substance—metallic or non-metallic—is represented by the characteristic rays of its individual spectrum. We have thus a composite spectrum, which may be considered as formed by the simple superposition of the spectra of its individual components.

The rays of the air in the condensed spark are much enfeebled in presence of the volatilised elements, especially when the explosive distance is very short; they are then reduced, practically, to the lines first signalised by Masson. These atmospheric rays have even the advantage of serving as marks for the position of the micrometric scale.

Without a condenser and with the coil alone we have, on the contrary, in the case of salts, complex spectra characteristic of the chemical species, and due probably to the non-dissociated molecule. They vary therefore from one compound to another. This fact has been already brought to light for salts, melted or dissolved, in numerous researches, especially those of A. Mitscherlich, Diacon, and Lecoq de Boisbaudran.

As a general method of investigation, and especially in the detection of the non-metals or in the examination of minerals, it is, in my opinion, really advantageous to make use of the condensed spark, the elements being always represented in it by the same rays, the principal of which are easily recognised at first sight.

In the case of salts the non-condensed spark gives, on the other hand, precise and very sensitive indications for detecting the presence of certain compounds by means of the band spectra.

It is, moreover, easy to suppress the condensation in the experimental arrangement employed.

For these researches we may make use of all coils; it is merely necessary to take condensers with surfaces much more considerable in proportion to the size of the coil than is generally done. For apparatus giving sparks of 3 to 5 c.m. in length, I use two, three, or four Leyden jars, each surface of which presents about 12 square decimetres.

It is curious to observe the effect of condensation upon the spark striking between electrodes coated with free non-metals: if the spark is condensed, it gives fine line-spectra of these substances *without* igniting them; if not condensed, it kindles them immediately, giving a continuous spectrum scarcely visible. This experiment is particularly striking with sulphur, arsenic, and selenium.—*Comptes Rendus*, cxxi., p. 121.

ON A

PHYSICAL THEORY OF THE PERCEPTION OF COLOURS.

By GEORGES DARZENS.

In order to explain the perception of colours, Young, and subsequently Helmholtz, admitted that each fibre of the optic nerve which enters into a cone of the retina is composed of three fibrils, one of which is strongly excitable by the red and little by the green and the violet; the second strongly excitable by the green and little by the red and the violet; and lastly, the third is strongly excited by the violet and little by the red and the green.

This hypothesis accounts for the existence of three elementary colours; it equally explains a certain number of other facts, such as some peculiarities observed in dyschromatopsies, the phenomena of saturated colours, &c. But it is unable to explain many other facts not less important. Why should light having a wave-length of μ 0·620 strongly excite one of these fibres and have scarcely any effect upon the two others?

Here is a new theory of luminous perceptions which seems to me to agree better with the progress of physical optics and of physiology.

A luminous ray, after having traversed the different strata of the retina, impinges normally upon the pigmentary layer of this membrane; there it is reflected, and interferes with the incident ray. Hence we must have there in front of the pigmentary layer, and consequently in the actual thickness of the retina, a system of stationary waves distant by $\frac{\lambda}{2}$, as in the experiments of O. Wiener, or in those of Lippmann on the photography of colours. It is further probable that these stationary waves can exist only in a feeble thickness, on account of the absorption by the medium which constitutes the retina.

Let us remark, in passing, that this specular function of the pigmentary layer exists in an unquestionable manner in the ox, where it constitutes the "carpet." These stationary waves excite the nervous terminations of the optic nerve. These terminations are of two orders, the rods and the cones.

The rods being constituted by cylindric fibrils, respectively parallel, we can conceive that the stationary waves will excite them all, whatever may be their position—that is, whatever may be the λ of the incident light. Hence we conclude that the rods give to the brain the general notion of light, without enabling us to judge of its colour. We know that the brain always conveys its excitements to the circumference, whatever may be the place where the nerve has been excited.

The cones, on the contrary, being formed of fibres, parallel, but unequal in length, will be excited differently according to the λ; they will enable the brain to take account of the colour.

These two conclusions are fully verified by experiment.

It is known that we do not perceive all the colours well except by the central part of the retina (the yellow spot). Now it is there where the cones are found, the rods being turned towards the equator of the retina, which gives merely the sensation of light without the notion of colour.

On the other hand, nocturnal animals which do not distinguish colours have no cones, whilst in birds which feed on coloured insects the retina is rich in cones.

Finally, if this theory is correct, whenever the pigmentary layer disappears, whether by old age or disease, there must result a parallel enfeebling of sight (a chromatopsy). This is apparently confirmed by experience,

This new theory can be brought to harmonise with the hypothesis of Young and Helmholtz. We need merely admit that the fibrils of the cones are divided into three groups proceeding to three different centres of perception. Still more, it explains why the wave-length which strongly excites one of these groups of fibrils must excite the other two groups feebly. It explains that curious arrangement of the retina when the excitable elements (cones and rods) are found placed in the deepest stratum, turned, so to speak, away from the side of the pigmentary layer which has hitherto appeared inexplicable.

It is remarkable to note that the procedure employed by the eye, in taking account of the wave-length of a ray of light, is quite comparable with the procedures hitherto employed by physicists.

To me this theory appears satisfactory to reason, since it reduces the perception of colours to the appreciation of a wave-length which is a magnitude of an order comparable to the dimensions of the anatomical elements of the retina. It further seems to me to throw a clear light on the explanation of a number of the peculiarities of the eye.

To cite merely a single instance, in the study of the achromatism of the eye we must no longer consider the retina as a simple screen like those of our laboratories, but a screen which perceives the different colours in different zones.—*Comptes Rendus*, cxxi., p. 133.

ILLUMINATION BY LUMINESCENCE.

By A. WITZ.

Luminous foci are constituted by an incandescent solid or liquid, the temperature of which, according to Draper, must exceed 1100°, in order that the light may be white and the spectrum complete. The visible has for its boundaries the wave-lengths 0·38 and 0·76 μ, but the infra-red extends, so to speak, indefinitely towards the less refrangible radiations, giving out a heat sensible to Langley's bolometer as far as to waves of the length of 30 μ, and consequently including more than five octaves of luminous radiations. If we trace the curve of energy of the spectra, plotting out the wave-lengths as abscissæ, and the intensities of the radiations as ordinates, we find that it presents only a single maximum, situate generally at the beginning of the infra-red, but which is displaced progressively and advances towards the most refrangible region as the temperature of the focus increases. This curve is not symmetrical with reference to the maximum ordinate, and the greater part of its area lies on the side of the dark heat-spectrum. A large proportion of the energy belongs, therefore, to these invisible and hot radiations. This is the reason why foci of light are all at the same time foci of heat, the photogenic yield of which is extremely slight. I have calculated this yield in a paper inserted in the *Comptes Rendus* (cxii., June 29, 1891).

To improve this yield would be an important scientific discovery, and a great number of investigators have made it the object of their researches.

It has appeared to some that the solution of the problem might be furnished by luminescent foci, in which the temperature of the rarefied gas is, according to Herr Warburg, included between 21° and 132°. These foci, it must be admitted, radiate but little light, but their thermic emission is still more feeble.

The luminescence of the tubes is effected either by the high tension currents given by Volta-Faradaic induction apparatus, or by the currents supplied by a Holtz machine. In the former case we may determine the watts consumed in the tube; in the second case we measure the kilogrammeters expended to set the generating machine in action, both when at liberty and when burdened.

I have experimented with several tubes, and especially with a lamp intended for miners and a tube for physicians (for illuminating deep cavities of the body).

The lamp for miners is illuminated without difficulty by the induction current of a small Ruhmkorff coil, yielding a spark of 20 m.m.; it yields enough light to read a table of logarithms at the distance of 40 c.m. from the source of light. Mr. Langley has been content with this very rudimentary photographic measurement. The pale greyish blue tint of the light does not lend itself to the methods of comparison used in photometry. I have found between the terminal electrodes a difference of potential of 4190 volts, the current having then an intensity of 0·27 milliampère, which makes 1·13 watt. The energy consumed is large in comparison with the light produced; we might hope for a better yield.

The results obtained with a Holtz machine are more interesting. I have used Hirn's transmission dynamometer to determine the work necessary to make the glass plate of the machine rotate 726 times per minute, under the following conditions:—

	Movement.				
	Free.	Closed circuit on machine.	Sparks of 145 m.m. 8 per second.	Miner's lamp.	Medical tube.
Work per second in kilogrammeters	1·043	1·785	2·174	1·711	1·763

Hence the illumination of the miner's lamp requires 1·711 − 1·043 = 0·668 kilogrammeters, or 6 6 watts. The yield is still less than that above. The incandescence of a lamp with a carbon filament in a vacuum only requires 3 watts per candle. Our miner's lamp absorbs more energy and gives much less light—a ruinous method of lighting. Still the quantity of heat radiated is slight.

Having plunged the medical tube into a calorimeter, we have observed a liberation of 0·00033 cal. per second, which corresponds to 0·00033 × 425 = 0·140 kilogrammeter. Now, the illumination of this tube requires 0·720 kilogrammetre, whence the heat produced corresponds only to the fifth part of the energy expended. From this point of view no other source of light gives so favourable a result.

The figures which we produce are evidently only a first approximation, since they vary with the nature and the form of the tubes employed, and have no absolute character. But we may learn from our experiments that, in lighting by luminescence, the proportion of thermic energy with reference to the entire energy is smaller than in any other source of light. By reducing to a minimum the losses of electricity, by concentrating the light in a limited space, by utilising the fluorescence of certain substances, by inventing certain special arrangements, we may hope to obtain foci the photogenic yield of which will be greater than that of our best sources of light. At present luminescence at low temperatures gives but very mediocre results, but at least enables us to reduce the invisible and useless portion of emission spectra.—*Comptes Rendus*, cxxi., p. 306.

ANG-KHAK, A CHINESE FUNGOID PIGMENT USED FOR COLOURING ARTICLES OF FOOD.

By H. C. POINSEN.

This colouring-matter is imported into Java from China, for giving a fine purple colour to foods and beverages. It is the product of a special fungus which is propagated in the province of Quant-tung for preparing the colouring-matter. Rice, thoroughly boiled, is spread out upon plates to cool, and when quite cold is sprinkled over with ang-khak of a former preparation. The plates, with their contents, are then kept for six days in a dark, cold place. It then has a red colour, which afterwards becomes darker.

In what manner the Chinese obtained the first ang-khak fungi is unknown. The colouring-matter dissolves readily in alcohol with a splendid garnet-red colour. The fungus belongs to the group of the Telebolæ. It vegetates upon any kind of carbohydrate in the presence of oxygen. The chief difficulty in its preparation is to keep away other fungi and bacteria, especially a species not yet examined. This is effected by means of a trace of arsenic, which prevents the growth of other bacteria without interfering with the development of the ang-khak.

The colouring-matter can be extracted with chloroform. In a state of purity it dissolves in methyl- and ethyl-ether, glacial acetic acid, aceton, and ethyl acetate, but very sparingly in water and dilute acids, and not at all in benzene, petroleum ether, oil of turpentine, carbon-disulphide, and glycerin. It melts at 50°, and at a strong heat it is decomposed without subliming. The alcoholic solution displays a narrow absorption band at D, and a broad band in the blue between D and G. The colouring-matter behaves like most of the aniline colours, but it is distinguished by its precipitability with mercuric oxide.

(The manufacture of ang-khak is probably the first instance of the technical use of microbia).—*Chemiker Zeitung.*

PREPARATION AND PROPERTIES OF HYDRAZIN HYDRATE.

By C. A. LOBRY DE BRUYN.

The isolation of hydrazin hydrate without the use of silver vessels is effected as follows:—

The commercial hydrate is first converted into the more readily soluble hydrobromic compound by means of barium bromide; the precipitate is filtered off, and the filtrate is concentrated by evaporation and gradually mixed with the calculated quantity of concentrated potassa lye. After the liquid has been diluted with an equal volume of alcohol it is allowed to cool; the potassium bromide is filtered off with the aid of the pump, rinsing out with a little alcohol. The filtrate is distilled at ordinary pressure until the ebullition point reaches 108°. We have thus the chief part of the base in the residue, in which potassium bromide further separates out on cooling.

After filtration it is distilled at first at the ordinary pressure, and then at a pressure of 121 to 122 m.m. Of the six fractions collected the three last contain from 77 to 97·5 per cent of hydrazin hydrate. To this mixture there is added, after heating to 50°, rather more than the calculated quantity of barium oxide to combine with the water present, when a strong heat is developed. After cooling there is added, to each 150 grms. of the hydrazin sulphate employed, 20 to 25 c.c. of absolute alcohol; it is filtered and washed with a little absolute alcohol. The solution is then fractionated at a reduced pressure, when about 22 per cent of the theoretical yield contains 99·7 per cent of hydrazin hydrate, free from silicon.

The boiling-point of hydrazin hydrate, at a pressure of 26 m.m., is constant at 47°. There is no perceptible decomposition. In air free from carbonic acid, hydrazin hydrate is slowly oxidised with an escape of gas. The substance dissolves various salts, such as potassium bromide, iodide, and cyanide; ammonia, sodium chloride, and salts of lead with difficulty, whilst potassium and zinc sulphates are scarcely taken up at all. Sulphur is gradually dissolved, even by dilute solutions; salts of lead gives a black deposit with the solution.

On boiling hydrazin hydrate at 22·8 per cent with sulphur the liquid takes a reddish-brown colour, whilst sulphuretted hydrogen escapes. From this solution sulphur is thrown down, not by water, but by an excess of hydrochloric acid. Phosphorus acts slowly upon hydrazin hydrate, and an odour of hydrogen phosphide is given off. Sodium decomposes hydrazin hydrate with the formation of hydrogen and ammonia, and there separates out a crystalline substance soluble in water and alcohol. The solution of the substance gives the hydrazin reactions. —*Rec. Trav. Chim. des Pays Bas* and *Chem. Zeitung.*

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.*

By F. W. CLARKE.

(Continued from p. 95).

Barium.

Richards has corroborated his earlier determinations of the atomic weight of barium, which were made with the bromide, by means of additional series of experiments upon the chloride (*Proc. Amer. Acad.*, xxix., 55). The work was carried out in the most elaborate and thorough manner, and for details the original paper must be consulted. First, barium chloride was titrated with standard solutions of silver, and the several series represent different methods of ascertaining accurately the end point. The data are as follows, with the ratio $Ag_2 : BaCl_2 :: 100 : x$ in the third column.

First Series.

Wt. Ag.	Wt. $BaCl_2$.	Ratio.
6·1872	5·9717	96·517
5·6580	5·4597	96·495
3·5988	3·4728	96·499
9·4010	9·0726	96·507
0·7199	0·6950	96·541
	Mean ..	96·512

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* From the *Journal of the American Chemical Society*, vol. xvii., No. 3. Read at the Boston Meeting, Dec. 28, 1894.

Second Series.

6·59993	6·36974	96·512
5·55229	5·36010	96·539
4·06380	3·92244	96·522
	Mean ..	96·524

Third Series.

4·4355	4·2815	96·528
2·7440	2·6488	96·531
6·1865	5·9712	96·520
3·4023	3·2841	96·526
	Mean ..	96·526

Fourth Series.

6·7342	6·50022	96·525
10·6023	10·23365	96·523
	Mean ..	96·524

All the weights represent vacuum standards. From the four series the atomic weight of barium is deduced as follows; when $O = 16$.

First series .. .. Ba = 137·419
Second " .. .. " 137·445
Third " .. .. " 137·449
Fourth " .. .. " 137·445

In three more series of experiments Richards determined the ratio between $2AgCl$ and $BaCl_2$. The data are subjoined, with the ratio $2AgCl : BaCl_2 :: 100 : x$ appended.

First Series.

Wt. AgCl.	Wt. $BaCl_2$.	Ratio.
8·7673	6·3697	72·653
5·1979	3·7765	72·654
4·9342	3·5846	72·648
2·0765	1·5085	72·646
4·4271	3·2163	72·650
	Mean ..	72·649

Second Series.

2·09750	1·52384	72·650
7·37610	5·36010	72·669
5·39906	3·92244	72·650
	Mean ..	72·6563

Third Series.

8·2189	5·97123	72·6524
4·5199	3·28410	72·6587
	Mean ..	72·6555

Hence we have for Ba—

First series .. .. .. Ba = 137·428
Second " .. .. .. " 137·446
Third " .. .. .. " 137·444

The mean of all is 137·440, as against 137·434 found in the work on the bromide. By combining the two chloride ratios, $Ag_2 : BaCl_2$ and $2AgCl : BaCl_2$, the ratio $Ag : Cl$ can be computed. This gives $Ag = 107·930$, a value identical with that of Stas.

(To be continued).

Detection of Ergot in Bran.—The method of E. Hofmann, according to Ulbricht, is useless if bran contains the seeds of *Polygonum convolvulus.* The author finds that 0 2 per cent of ergot, and even smaller quantities, can be detected microscopically if the bran is previously digested for two hours on the water-bath with sulphuric acid at 1·25 per cent, then with soda-lye of the same strength, and, lastly, treated in the cold with absolute alcohol and ether.—*Zeit. Anal. Chem.*, xxxiii., Part 6.

THIRTEENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature presents to the Chemical Section its Thirteenth Annual Report.

During the twelve months which have elapsed since the last report the following bibliographies have been printed: —

1. "Indexes to the Literature of Cerium and Lanthanum." By W. H. Magee. *Smithsonian Miscellaneous Collections*, No. 971. Washington, 1895. 43 pp. 8vo.

2. "Index to the Literature of Didymium, 1842—1893." By A. C. Langmuir. *Smithsonian Miscellaneous Collections*, No. 972. Washington, 1895. 20 pp. 8vo.

These bibliographies of three associated metals fill an important gap in chemical literature. That by Dr. Langmuir is reprinted from the *School of Mines Quarterly* (vol. xv.), at the request of your Committee. Both indexes are arranged chronologically and provided with author-indexes.

3. "Bibliography of Aceto-Acetic Ester." By Paul H. Seymour. *Smithsonian Miscellaneous Collections*, No. 970. Washington, 1894. 148 pp. 8vo.

This bibliography was compiled by the author under the direction of Prof. Albert B. Prescott, and by him submitted to the Committee who recommended its publication Aug. 22, 1892. It consists of a series of carefully prepared, critical abstracts of original papers arranged chronologically with author- and subject-indexes.

After issuing the twelfth Annual Report the attention of the Committee was directed to two contributions to the bibliography of chemical and pharmaceutical periodicals by Dr. Friedrich Hoffmann, editor of *Pharmaceutische Rundschau*, viz.:—

4. "Die Deutsch-sprachlichen pharmaceutischen Zeitscriften." *Pharm. Rundschau*, New York, vol. xii., pp. 7—10 (Jan., 1894), and p. 28 (Feb., 1894).

5. "English-sprachliche pharmaceutische, chemische und botanische Zeitschriften Nord-Amerika's." *Pharm. Rundschau*, New York, vol. xii., pp. 131—136 (June, '94).

Several chemists have made reports of progress :—

Prof. Henry Trimble, of Philadelphia, states he continues to collect references to the literature of the Tannins with the expectation of further publication at no very distant date.

Prof. Arthur M. Comey reports that his "Dictionary of Solubilities," vol. i., is nearly all in type, and should appear early in the autumn.

Dr. Alfred Tuckerman expects to complete the MS. of his "Index to the Mineral Waters of all Nations" in a few months.

Prof. F. W. Clarke is making progress with a new edition of the "Re-calculation of the Atomic Weights."

Dr. H. Carrington Bolton reports having done much work on the Supplement to his "Bibliography of Chemistry," the MS. now comprising about 6500 titles.

Mr. C. LeRoy Parker, of the Columbian University, Washington, has undertaken an "Index to the Literature of Attempts to Decompose Nitrogen."

Mr. George Estes Barton, of the same Institution, is at work on a "Bibliography of Glycerol"; and Mr. George Baden Pfeiffer, also of the Columbian University, is engaged on a "Bibliography of Picric Acid and the Nitrophenols."

At the request of the Smithsonian Institution Dr. H. Carrington Bolton has undertaken to edit a new edition of his "Catalogue of Scientific and Technical Periodicals, 1665—1882," published in 1885 in the *Smithsonian Miscellaneous Collections.* The new edition will bring

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* Advance sheets from *Proceedings Amer. Assoc. Adv. Science*, vol. xliv., communicated by Professor H. Carrington Bolton.

down to date the old periodicals and include new ones established since 1882. The work is well under way.

Mr. W. D. Bigelow, of the Chemical Division of the U.S. Department of Agriculture, has completed the MS. of an "Index to Methods for the Detection and Estimation of Fusel Oil in Distilled Liquors." The channel of publication has not been determined.

In a communication to the chairman, Prof. W. Percy Wilkinson, of Melbourne, states he is engaged on an "Œnological Biography," to include works relating to the vine, viticulture, wine-making, vine-diseases, and wine-analysis, published in Germany, France, England, America, Italy, Portugal, and Spain. He expects the bibliography to number 2000 titles, and will give full dedetails as to date, size, editions, &c. It is to be published by the Royal Society of Victoria.

Monsieur G. Fr. Jacques Boyer, Editor of the *Revue Scientifique*, Paris, announces the preparation of a "Bibliography of Physical and Chemical Science"; information as to its scope and period is lacking.

Those interested in the chemical applications of electricity should note the following:—

"Elektrotechnische Bibliographie; monatliche Rundschau über . . . der Elektrotechnik." Von Georg Maas. Leipsig, 1893.

Also: "Leiner's Elektrotechnischer Katalog . . . von 1884 bis 1893." Leipsig, 1893. 8vo.

The following special bibliography has recently appeared in France:—"Bibliographie de la technologie chimique des fibres textiles. Propriétés, blanchîment, teinture, matières colorantes, impression, apprêts." Par J. Garçon. Paris, 1893. 8vo. This work has been honoured with a prize by the Société Industrielle de Mulhouse.

Although not pertaining to chemistry, we may briefly note the appearance of another special bibliography:—"Bibliographie der psycho-physiologischen Litteratur des Jahres 1893." Hamburg, 1894. 8vo. Published in the *Zeitschrift fur die Psychologie und Physiologie der Sinnesorganen.*

Attempts to establish a comprehensive Index to Chemical Literature in the form of a periodical are not altogether successful, lacking the important element of permanence. The "Index" announced by Dr. Bechhold, of Frankfort-on-Main, noticed in our Twelfth Report, has not made its appearance; the *Biblioteca Polytecnica*, by Szczepanski, ceased at the close of one year; the *Universal Index*, by Wien and Brockhaus, reached only nineteen numbers. Dr. J. Ephraim advertises the following, "Index der gesammten chemischen Litteratur (Wissenschaft und Technologie), Berlin," but no number has yet appeared.

Committee:—

H. Carrington Bolton, Chairman,
F. W. Clarke,
Albert R. Leeds,
Alexis A. Julian,
John W. Langley,
Albert B. Prescott,
Alfred Tuckerman.

August, 1895.

On Hexamethylenetetramine.—R. Cambier and A. Brochet.—Among the interesting properties of hexamethyleneamine, the authors mention the formation with bromine and iodine of the addition-compounds $C_6H_{12}N_4X_2$ and $C_6H_{12}N_4X_4$. The compounds with X_4, being very unstable, lose in part their haloid element on mere exposure to air. Nitrous acid reacts upon hexamethyleneamine and forms in the first place dinitrosopentamethylenetetramine, which is decomposed by acids and yields nitrogen, ammonia, and formic aldehyd. Hexamethyleneamine, if treated by acids, is easily split up by hydration into its components.—*Bull. Soc. Chim. de Paris*, xiii.-xiv., No. 4.

NOTICES OF BOOKS.

An Introduction to the Study of Disinfection and Disinfectants. Together with an Account of the Chemical Substances used as Antiseptics and Preservatives. By Samuel Rideal, D.Sc., F.I.C., F.C.S., &c. 8vo., pp. 316. London: Charles Griffin and Co., Lim. 1895.

The author of the work before us sets out with distinguishing between disinfectants, antiseptics, and deodorants, classes of substances often confounded. Charcoal he classes not among disinfectants, but with the deodorants. The problem of disinfection he shows is a struggle for existence between men and the pathogenic microbia, which, despite their minuteness, rank among our most formidable enemies. The methods of solving this problem are classed under the heads of exclusion, removal, and destruction.

Under the head of Mechanical Disinfection the author enumerates a number of substances used as filter-beds, or in the treatment of fœcal matters and of impure waters. It is mentioned that light has a destructive action on bacteria, and even to some extent on their spores. Hence, as Dr. Percy Frankland rightly insists, every opportunity should be used for insolation in the construction of water-works, and, we must add, of works for the treatment of sewage.

The value of charcoal, animal and vegetable, is duly recognised. The former is credited with removing the ptomaines and a number of other hurtful organic compounds. The action of certain residual carbons is very similar. The remark that "a large number of processes have endeavoured to recover the phosphate (of sewage) by using the sludge as a fertiliser, but they have all met with little commercial success," we must pronounce utterly mistaken. Soot is rightly said to have no great power, and coal-dust is with equal correctness proclaimed to be almost inert. The value of peat is fully recognised, but in the treatment of sewage care, we must urge, should be taken to avoid pyritic samples, such as those of some districts of Berks.

Sterilised sand, according to Fränkel and Piefke, does not retain microbia.

The Chamberland and Berkefeld filters—the latter made of infusorial earth, compressed and baked—are recommended for household use, but filters of stone and of asbestos are condemned, views which our experience enables us fully to endorse.

The process of Scott Moncrieff has been tried and abandoned at Aylesbury.

The process of disinfection by means of hot air and steam is described at some length, with the addition of illustrations showing the plant employed. Incinerators, or destructors for dust, &c., are also noticed.

The fourth chapter discusses chemical disinfectants. The opinions recorded concerning different agents and processes are far from agreeing. The Hermite process is judged unfavourably by Sir H. Roscoe and Lunt (p. 69), and by Dr. Kelly, the medical officer of health at Worthing, who incorporates the chemical and bacteriological analyses of Drs. Dupré and Klein. Chamberland and Fernbach allege that eau de Javelle (1 : 120) and commercial hydrogen peroxide are more effective than mercuric chloride against pathogenic microbia.

The important caution is given that sodium chloride is not a disinfectant, and that brine sometimes acquires a high degree of toxicity. This is the more important as we have observed that stale brine is often kept and used for salting successive quantities of bacon, hams, fish, &c.

On the comparative value of the halogens opinions differ.

On chloroform, which has even been proposed for the treatment of sewage, Dr. Rideal remarks that its cost and its poisonous action on animals render it of very limited application.

The author recognises that "polluted water flowing over weirs and waterfalls is oxidised and becomes clear and brilliant," and again that "the self-purification of rivers in this way is now accepted by most chemists, the natural aëration being aided by Infusoria and vegetation in removing most of the dead organic matter, and in reducing the number of micro-organisms present." These conclusions will meet with the approval of observant and unbiassed students of the sewage question.

Sulphate of lime is rightly condemned as an ingredient in mixtures for the precipitation of sewage. It has the serious disadvantage—not mentioned here—of injuriously affecting the health of the men employed in sewage-works. To find zinc salts still used in the disposal of sewage is deplorable.

The process Patent No. 11641 (1884), is travestied so as to give a very misleading impression of its nature. The summary of sewage precipitation processes given by Parkes and Corfield (p. 129) must be taken with a very large grain of salt.

We regret that we cannot further examine this able and interesting work. Its weakest side is its criticism of processes for the treatment of sewage.

Alkali, &c., Works Regulation Act, 1881. *Thirty-first Annual Report on Alkali, &c., Works by the Chief Inspector.* Proceedings during the Year 1894, presented to the Local Government Board and to the Secretary for Scotland. London: Her Majesty's Stationery Office.

This Report is drawn up with great care and accuracy, and contains both alarming and reassuring features. The number of works in England, Ireland, and Wales, as now registered, is 1056, of which only 102 are alkali-works proper, whilst 954 fall within the schedules of other establishments recently included under the provisions of the Act. Since 1893 there has been an increase of one alkali-works and nine other works. In Scotland there are 126 registered works, making a grand total of 1182.

The number of processes of manufacture which fall within the provisions of the Act is now 1520. The separate processes are:—Alkali, copper (wet process), sulphuric acid, chemical manures, gas liquor, nitric acid, sulphate and muriate of ammonia, chlorine and bleaching-powder, sulphur recovery, salt, cement, alkali waste, barium and strontium, antimony sulphide, bisulphide of carbon, Venetian red, lead deposit, arsenic, nitrate and chloride of iron, muriatic acid, fibre separation, tar and zinc smelting.

One most offensive process, of no national importance, has escaped attention,—to wit, ballast-burning, which, in most of the outskirts of London, fills the air with nauseating fumes, and which ought to be totally suppressed in all urban districts.

The visits of inspection to scheduled works are made about once monthly, unless there is apparent need for a closer investigation. In alkali works and sulphuric acid works definite limits are fixed as to the amount of acid fumes which may lawfully escape. In other cases the Act merely requires that the best practicable means for preventing the escape of noxious gases and vapours should be employed.

The Report shows that the amount of hydrochloric acid in the chimney gases is less than one-half, the limit allowed by law; whilst in case of sulphuric acid the escape is only about one-third of the legal margin. These facts are doubly satisfactory, as showing, on the one hand, that the standards fixed are reasonable, and, on the other hand, the watchful attention of the inspectors and the loyal compliance of the manufacturers.

Two successful prosecutions have been conducted and fines inflicted for evasions of the enactment that the inspector is to have full access to all apparatus used in carrying out the operations.

It is satisfactory to learn that the Leblanc works hold their own in virtue of the chloride of lime which they only are as yet able to produce.

The effects of the coal-strike of 1893 are still felt. The salt decomposed in the Leblanc process was in the year 1892 519,593 tons, but has now fallen to 434,298 tons. On the other hand, the salt consumed in the ammonia process has risen in the same time from 304,897 tons to 361,603 tons. Thus the gain of the ammonia process is far from explaining or compensating the decline of the Leblanc process. The electric alkali process, if the required energy has to be obtained from coal, is an amusing scientific version of the "House that Jack built." But the writer shows that where water power is cheap and abundant,—*e. g.*, Italy, Switzerland, South-eastern France, Norway, as well as the Dominion and the United States,—both Leblanc and Solvay may find themselves in jeopardy.

The ammonia lost by our wasteful system of coal-burning was estimated by Dr. Angus Smith at £50,000,000. A yearly economy in this direction, to the extent of £2,000,000, has already been secured.

In the treatment of tank-waste the Chance-Claus process works successfully. At Widnes, St. Helens, &c., raw waste is no longer deposited on the land—a subject for public congratulation. But old beds of tank-waste, where they have been used for filling up hollows and making embankments, still remain, and if they come in contact with acid leakage serious accidents may occur. A fatal case took place lately at Irvine, and is here recorded.

The manufacture of nitric acid is experiencing extension. Mr. Manning Prentice, of Stowmarket, has made the process continuous, thus effecting at once economy and a suppression of possible nuisance.

Coal-smoke is not a substance of which the inspectors under the Alkali Act have to take official cognisance. But they are obliged to examine it, as its effects are too often ascribed by the public to the emanations from chemical works. About a million tons of coal are burnt yearly at Widnes. This coal contains about 1½ per cent of sulphur, and thus generates 30,000 tons of sulphurous acid, which is diffused over the country. The effects of a sooty atmosphere and of sulphurous acid are rightly considered by Mr. Fletcher, the chief inspector, as taking no small share in the injury to vegetation. He thinks that the "open fire is incorrigible," and he fears that the love of an Englishman for the cheerful blazing fire will stand in the way of any reform. He mentions, however, the case of "one house, inhabited by a large family, where recently, during a week of frosty weather, twenty-one open fires and five oil or gas stoves were kept burning." He thinks that one of the twenty-one fires, if burnt in a properly constructed stove, would have heated the whole house better than the twenty-one in open grates.

In a passage quoted from *Die Chemische Industrie*, on the health of the workmen employed by the Griesheim Chemical Co., it is declared, on the authority of Dr. C. Wolff, for ten years medical officer to the works, that—"As in former years, artisans such as carpenters, coopers, smiths, &c., show a higher percentage of sickness than the process men," *i. e.*, those employed in the manufacture of sulphuric acid, hydrochloric acid, nitric acid, soda-ash, caustic soda, nitrobenzene, picric acid, chromates, &c.

We have every reason to conclude that the present Chief Inspector, Mr. A. E. Fletcher, and his colleagues are proceeding on the lines laid down by his distinguished predecessor, Dr. R. Angus Smith.

Report of the Dairy Commissioner of the State of New Jersey. For the Year 1894. New Jersey: Trenton.

This Report will be of the greatest value to sanitary chemists. We find that in the United States the liability of milk to pollution and its danger to public health are fully recognised by the Courts, by men of Science, and even by the general public. We fear that in this last respect we, in this country, do not hold the first rank. Strict legislation and analytical skill, chemical and microbiological, fall short of their aim unless supported by enlightened public opinion.

But in America very much remains to be done. We learn that "the standard of 12 per cent solids is so low that most whole milk can be watered—and much is—with great precision, so as just to escape the penalties of the law." In Hudson and Essex counties nearly 2500 stables were found by the inspectors, in most of which the cattle were kept in a crowded and unhealthy condition, and in which the principal food was wet and soured brewers' grains. The Commissioner proposes raising the standard to 12·5 per cent total solids, with a minimum of 3·5 per cent of fat.

The importance of cleanliness in cow-houses and dairies is now beginning to be appreciated. In some establishments the cattle are groomed previous to milking; their udders are washed; the milkman is required to exchange his ordinary working clothes for a clean-washed smock, and to wash his hands and remove the offensive dirt from his finger-nails (which is otherwise—*horribile dictu*—washed out by the warm milk and carried into the pail). But even this improvement falls short of what is needed. It is truly remarked that when straw becomes damp and filth-stained, and then raised to the temperature of blood-heat by the cattle lying upon it, such straw becomes a most prolific breeding-ground for bacteria. "Every movement of the cow and the milkman raises up a cloud of bacterial dust from the bedding, and until a substitute is provided this dust will continue."

It may be asked whether peat-litter might not be found in this respect preferable to straw? It is proposed to dispense with bedding altogether, and let the cows lie on a clean inclined plank floor, made waterproof and with the seams caulked, all excreta being forthwith removed.

An interesting fact here mentioned is that, with a nearly identical food, the best cow produced 2½ times more milk and 3 times more butter than the poorest cow (referring to certain experiments performed at Kildebrönde, in Denmark).

From facts ascertained we learn the importance of refrigerating milk before being conveyed to consumers.

Mention is made of pasteurised milk, of sterilisation, and of a "certified milk" the preparation of which has been described in a former report, and in which the number of bacteria per c.c. is only a few hundreds instead of from 10,000 to 60,000 bacteria. The alleged sterilisation is sometimes illusive.

None of the brands of condensed milk here described are known in Britain.

The Pharmaceutical Journal of Australasia. Vol. VIII., No. 5.

The interesting fact in this issue is the opening of chemical works by Messrs. Elliott, at Brisbane. The immediate object of the firm is the production of sulphuric acid, the freight of which from Britain may be considered prohibitory. No information is, however, given as to the supply of pyrites, its quantity and quality.

Ulterior objects of the firm are the manufacture of potassium cyanide, the nitrogenous matter being the refuse from the meat works; the production of compressed carbonic acid, and that of superphosphate. For all these products there cannot fail to be a large opening in Australia.

The Atomic Weights of Nickel and Cobalt.—Clemens Winkler.—The author finds the atomic weight of nickel, as calculated from the mean result of his experiments, 58·7433, and that of cobalt 59·3507. These atomic weights are referred to H = 1 and I = 126·53.—*Zeit. Anorg. Chemie.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 6, August 5, 1895.

Illumination by Luminescence.—A. Witz.—(See p. 104).

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 4, 1895.

Nickel and Cobalt Sulphides.—A. Villiers.—Already noticed.

Qualitative Separation of Nickel and Cobalt.—A. Villiers.—Already noticed.

Protomorphic States of Zinc and Manganese Sulphides.—A. Villiers.—Already noticed.

Researches on the Basic Nitrates.—M. Athanesco.—The author finds that the process of which he has spoken in a former paper is not novel, but had been previously employed by other chemists. His objects have, however, been different. He seeks to show that the basic compounds contain hydroxyls attached to the metals which they completely saturate, and that very often in the conditions of the formation of the basic salts the plurivalence of the atoms takes always a preponderating part in the direction that, in place of obtaining compounds derived from anhydrides of the first, second, or third degree, we may obtain them corresponding to the highest degree of hydration of the non-metal. He turns his special attention to the lead nitrates.

On the 2-Ethyl-4-Methylpentanoïc Octylic Acid.—Ph. A. Guye and J. Jeanprêtre.—Not adapted for useful abstraction.

Active Amylacetic Acid and some of its Derivatives.—Mdlle. I. Welt.—The chief result of these experiments relates to the ethers of amylacetic acid. If we calculate the values of the product of asymmetry of the methylic and ethylic ethers, we find decreasing numbers; it is the same with the rotatory powers. We cannot, then, meet with in this series an ether with a maximum rotatory power, as the first term is already on the descending branch of the curve.

Contribution to the Study of the Tartaric Ethers.—Ph. A. Guye and J. Fayollot.—Already noticed.

New Process of Preparing α-Naphtholsulphonic Acid, $C_{10}H_6.OH.H.SO_3$ 1-4.—Fred. Reverdin.—None of the procedures hitherto employed are founded upon the direct sulphonation of α-naphthol. The author and his colleague, De la Harpe, have found the carbonic ether of α-naphthol an excellent primary material for the preparation of naphtholsulphonic acid 1-4. In the industrial production, carbon oxychloride is passed at the common temperature into a solution of—

α-Naphthol.. ..	60 kilos.
Soda-lye	60 ,,
Water	1000 ,,

Sulphonated Colouring Matters derived from Triphenylmethane.—Maurice Prud'homme.—The author's experiments establish the complete parallelism between the series of rosaniline and its derivatives and the corresponding series of sulphonated rosaniline, and support the constitutional formulæ which Rosenstiehl has proposed for these two classes of substances. All the properties of magenta which I have pointed out re-occur in the bases of malachite green and of hexamethylated violet. All those of acid magenta re-occur in acid green and magenta and in Nicholson blue. The alkaline salts of sulphonated, diamido, and triamido triphenylcarbinols are colourless.

These substances may be considered as hydrated organic bases. The salts of these bases, where the hydroxyl may be replaced by an acid radicle, are coloured. Acid magenta is, or may be, according to proportions of hydrochloric acid added to the colourless alkaline salt, a mixture of $HO—C\equiv(C_6H_3.SO_3Na.NH_2)_3$ (colourless) and of coloured $Cl—C\equiv(C_6H_3.SO_3NaNH_2)_3$, or even of this latter body and $Cl—C\equiv(C_6H_3.SO_3H.NH_2)_3$ (coloured).

Insufficiency of Kjeldahl's Method for Determining Nitrogen in the Chloroplatinates.—M. Delépine.—Already noticed.

No. 7, 1895.

This issue contains a long notice of the life and researches of E. A. Rigout, a distinguished chemist who died in August last at the age of seventy-five. During the year 1871 he had remained alone in charge of the École des Mines, and at no small risk to his life he contrived to save this establishment from destruction.

On the Cryohydrates.—A. Ponsot.—After a careful and prolonged examination the author concludes that the cryohydrates of Guthrie do not exist, but are merely mixtures of pure ice and of a solid salt, hydrated or anhydrous.

Influence of Temperature and of the Ambient Medium on the Transformation of Amorphous Zinc Sulphide.—A. Villiers.

Method of Determining the Crystallisation of Precipitates, Zinc and Manganese Sulphides, Manganese Hydroxide.—A. Villiers.—Already noticed.

Oxides and Sulphides having an Acid and a Basic Function. Zinc Sulphide.—A. Villiers.—The study of the properties of oxides and sulphides has led us to think that the acid and alkaline functions which may be fulfilled by indifferent oxides and by some sulphides do not belong, at least in a number of cases, to one and the same substance, but to two varieties, distinct in their chemical and physical properties. In the case of precipitated zinc sulphide, we may distinctly recognise the existence of two varieties.

Analytical Characters of a Mixture of Barium, Strontium, and Calcium Salts.—H. Baubigny.

Non-Existence of the Mixed Anhydrides.—L. Rousset.—When proceeding on the usual method the author has obtained merely a mixture of two anhydrides. This was found to be the case with the alleged acetyl-butyric, acetyl-valerianic, and acetyl-benzoïc acids.

Action of the Asymmetric Ketonic Compounds upon the Primary Aromatic Amines.—Louis Simon.—In the action of pyruvic acid upon a primary aromatic amine, there are formed simultaneously several compounds, but they are neither stereoisomers nor even structural isomers.

Action of the Chlorides of Acids upon Hexachlorophenol-*a* in presence of Aluminium Chloride. Formation of Ethers of Pentachlorophenol.—E. Barral.

Action of Aluminium Chloride on *a*-Hexachlorophenol.—E. Barral.—These two memoirs are not adapted for useful abstraction.

On Piperonylidene-acetone.—L. Rousset.—If 20 grms. of pure piperonal, regenerated from its bisulphite, are dissolved in 50 grms. dimethylketone, and if to this solution there are added 500 grms. water and 50 grms. soda at 10 per cent, on stirring the mixture heats, and there is produced a light yellow precipitate. This precipitate, if re-crystallised from alcohol, forms the compound in question.

Compound of Hexamethyleneamine with Bismuth Iodide.—M. Delépine.—This compound contains—Bismuth, 16·83; iodine, 58·24; nitrogen, 7·35; and water, 5·82 per cent.

On Hexamethyleneamine. (Further Continuation).—M. Delépine.—An account of the salts of the ammoniums:—The iodamylate, the action of acids, and the formation of primary amines.

On Hexamethyleneamine. (A Continuation).—M. Delépine.—The author describes here the solubilities, the hydrate, bromide, sulphate, and phosphate.

Oxidising Power of Laccase.—G. Bertrand.—The author has obtained from the latex of the lac tree of Tonkin a new soluble ferment, which he names laccase. This new ferment has the specific character of setting up the direct oxidation of the substances upon which it acts. It is thus distinguished from all the ferments previously known which occasion merely hydration and splitting up. The results cannot be ascribed to the action of micro-organisms, as the media in which the experiments were conducted were antiseptic,

Watering Milk. Its Detection by an Examination of the Whey.—H. Lescœur.—Every sample of milk which gives a serum of specific gravity below 1·027, and the solid matter of which does not amount to 67 grms. per litre, may be declared as "watered."

THE CHEMICAL NEWS.

VOL. LXXII., No. 1867.

(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

PERHAPS a majority of the students to whom we venture to address our annual remarks look forward to the utilisation of the knowledge they are acquiring in some art or manufacture with which they hope to be specially connected; but there are others—too many we fear—who regard chemistry as the basis of an independent profession. Such men, in Britain, labour under the inconvenience of having as a body no recognised and distinctive name. In France they would be known as "Chemistes," and in Germany as "Chemiker," but the English equivalent of these terms has been in our country appropriated by the profession who are more suitably known in France as "Pharmaciens" and in Germany as "Apotheker," but who, with us, show no disposition to abandon the name of chemists. Nay, if "Tom Brown's" exposition of the law be correct, even such qualified designations as "analytical chemist" are the exclusive property of the compounders and dispensers of medicines. Some suggest the name "Analysts," which, however, connotes only a portion of the functions of the profession whose cause we are pleading. Professor Huxley, were he still living, might perchance have invented for us an unobjectionable name, which for the present must be allowed to stand over as a desideratum.

Concerning the relative rank of the profession our esteemed contemporary the *Chemiker Zeitung* is much exercised. It contends that if all chemists before being entitled to exercise their profession were obliged to pass a "Staat's examen," after their University career, they would no longer be regarded as inferior (!) to engineers and lawyers. What effect such an examination might have upon German public opinion we cannot presume to decide. But in the opinion of the world German chemists rank incomparably higher than any lawyers or engineers. No names among the latter classes carry with them the spell which adheres to the names of Liebig, Wœhler, Bunsen, or Hofmann. We are painfully conscious that in Britain, as no doubt also in Germany, the emoluments of the lawyer and of the engineer exceed those of the chemist. With us neither the engineer nor the chemist is a State-official. The latter is indeed relatively poor, since when he gives advice, whether to a private firm or to a public body, he is not paid by a percentage on the outlay which his schemes necessitate. Could he claim a percentage on the economy which he renders possible, he would be a more prosperous man than he is at present. Moreover, he is beset with difficulties to which, *e.g.*, the engineer and the lawyer are strangers. He is, if we may use the expression, trespassed upon in all possible directions. As an instance, the difference between pure water and contaminated water is purely chemical and micro-biological. Only the chemist and the micro-biologist can appreciate such difference, can know how to encounter it, and can judge if and in how far the methods used are successful. Yet, when the treatment of the sewage of London was under discussion, it was actually suggested that the engineer who had designed the Forth bridge—a matter purely mechanical—should be consulted! Why, had he even succeeded in building a railway across the Straits of Dover, that fact would have been no evidence of his power of purifying a single gallon of sewage. It is a strange thing that the Rivers' Pollution Commission included only one chemist to two engineers, and no microscopist or physician. In a very like manner, when question arises before any municipal body concerning the treatment of polluted waters, it is forthwith proposed to consult some eminent *engineer*.

But the chemist fares almost as badly at the hands of the legislature and its officials as does the experimental physiologist. The ukase ordering the addition of coal-naphtha to methylated spirits still exists, and causes a great hindrance to scientific research. The addition of a mere trace of Dippel's animal oil—as it is sanctioned by the German law—would have rendered the spirit more thoroughly undrinkable, without inflicting such annoyance on the chemical manufacturer and the scientist engaged in research. It further appears that a chemist is, strictly speaking, liable to a tax on every retort, &c., in his laboratory, of what material soever, and however incapable of being used for the illicit distillation of spirits.

Further, there is a chronic agitation kept up by some medical men(especially medical officers of health) and by a few pharmacists, to encumber the sale of the ordinary mineral acids with red-tape precautions. Any such enactment cannot have other than an unfavourable action upon chemical research. "Free research" should be the watchword of every man of Science, and it is in the long run essential to the welfare of the community.

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 £2 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 £1, 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 commence on the third Monday in July.

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 Exmination 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 on the third Monday in October.

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, Tuesday, and Wednesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday and Wednesday 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 Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and 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, with reference both to the special subject selected by him and to the Thesis.

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.

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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.

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, 1894; 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.

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 £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, 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.

(Division of Engineering and Applied Science).

Professor of Chemistry.—J. M. Thomson, F.R.S.E., F.C.S.

Demonstrator of Practical Chemistry.—Herbert Jackson, F.C.S.

Assistant Demonstrators.—P. H. Kirkaldy and W. H. Sodeau.

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 Division 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 mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 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 1895-96, are Tuesday, October 1, Wednesday, January 15, and Wednesday, April 22.

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.—Morris Travers, B.Sc., and N. T. M. Wilsmore, M.Sc.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Wednesday, October 2nd, until Friday, December 20th;

Second Term, from Tuesday, January 14th, 1896, till Friday, March 27th;

Third Term, from Tuesday, April 21st, till Wednesday, July 1st. Class Examinations begin on June 18th.

Junior Courses.

First Term: Tuesday and Thursday at 11, and Saturday at 10. Third Term: Tuesday and Thursday at 10, Friday at 4. 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: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

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, beginning on January 14. 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; 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 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.; for a Second Course, £3 3s.

Practical Class.

First and Second Terms, Tuesday and Thursday, at 11.

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.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1895-96; also the Clothworker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor.—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor.—W. P. Wynne, D.Sc., A.R.C.S.

Demonstrators.—H. Chapman Jones and J. W. Rodger, A.R.C.S.

Assistants.—G. S. Newth, W. Tate, A.R.C.S., and A. Eiloart, Ph.D., D.Sc.

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 Royal 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. Students who are not candidates for the Associateship are permitted to enter as occasional students 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 2nd 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 the third year 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. Model and Freehand Drawing, £1 per term. Descriptive Geometry, £3 per session. Mine Surveying, £10.

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 fees.

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 and Art Directory may obtain permission to attend free any course of lectures.

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 third class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science and Art Directory.)

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-fourth Session will commence on Wednesday, October 2nd, 1895. Entries not previously arranged with the Dean or Secretary may be made between 10 a.m. and 1 p.m. on that day.

Professors and Lecturers.—Prof. Dunstan, M.A., F.R.S., Sec. C.S., F.I.C., Chemistry; Prof. Attfield, Ph.D., F.R.S., F.I.C., Practical Chemistry; Prof. Green, Sc.D., F.R.S., F.L.S., Botany (Dean); Prof. Greenish, F.I.C., F.L.S., Materia Medica; Mr. Joseph Ince, F.L.S., Pharmacy and Practical Pharmacy.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of March. An Advanced Course of Lectures on Organic Chemistry begins in April and extends to the end of June. The lectures will be given at 9.30 a.m. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. A bench in the chemical laboratories, which are open daily throughout the Session, can be engaged for any period. 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.

Prospectuses and further information may be obtained from Mr. Ernest J. Eastes, F.I.C., Secretary to the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

University of Wales.

Professor.—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Gœttingen), F.I.C.

Assistant Lecturer and Demonstrator.—A. W. Warrington, M.Sc. (Vic.)., F.I.C.

Assistant Lecturer in Agricultural Chemistry.—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Monday, September 30, 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; four lectures weekly during the Lent and Easter Terms. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4) B.Sc. Course; three lectures weekly throughout the Session. (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 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, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

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 17, 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.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

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, F. V. Dutton.

Physics.—Professor, Andrew Gray, M.A., F.R.S.E.

The Session opens October 2nd, 1895. 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, £2 2s.

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.

Demonstrators.—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 7th, and terminates on June 26th, 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 Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held.

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 5; 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 Board 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 Women 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 1895-96 will begin on October 4th. 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 have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of 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.

Advanced Course.—One Lecture a week will be given throughout the Session.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given during the Second Term, and three Lectures a week during the Third Term. 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.

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 COLLEGE, BIRMINGHAM.

Professor.—Percy F. Frankland, Ph.D., B.Sc., F.R.S.
Assistant Lecturer.—C. F. Baker, Ph.D., B.Sc.
Demonstrator.—D. R. Boyd, B.Sc.

The Session will be opened on October 1st, 1895.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. Lecture days—Wednesdays and Fridays at 11.30.

Persons entirely unacquainted with Chemistry are recommended to attend this Course before entering for the General Course. Candidates for the Matriculation Examination of the University of London also are advised to attend this Course.

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. May to July (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, Wednesday, and Friday at 11.30 a.m. Fee, £1 11s. 6d.

The General Course (including Inorganic and Organic lectures) qualifies for graduation in the medical faculties of the universities of Edinburgh, Glasgow, Aberdeen, and Durham.

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 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 of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given by Mr. McMillan, 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.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of £100 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of £100 is awarded annually in September.

Forster Research Scholarship.—A Scholarship of the value of £50 is annually awarded.

For particulars apply to the Registrar.

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 or Lecturer.

BRADFORD TECHNICAL COLLEGE.

Chemistry and Dyeing Department.

Professor.—(Vacant).

Demonstrator.—(Vacant).

Lecturer on Botany and Materia Medica.—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 16th 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, F.I.C., 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.—A. C. Wright, B.A., and T. Ewan, Ph.D., B.Sc.

The Session begins October 8, 1895.

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 12 noon Fee £3 13s. 6d.
5. Organic Chemistry Honours Course. — Wednesday and Friday at 12 noon. 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.
9. Chemistry for Teachers.—Saturdays from 9.30 to 12.30 in the first and second terms. Fee, £4 4s.

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, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—Tuesdays, 9.30 to 11.30 October to end of December; Thursdays, 2 to 4 from January to end of March.

Practical Course in Sanitary Chemistry.—At times to be arranged.

Practical Organic Chemistry for Medical Students.—At times to be arranged.

Evening Class.

A Course of twenty Lectures by Mr. Ingle, on the Chemistry of Combustion will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 10. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.I.C.

Lecturer and Research Assistant. — A. G. Perkin, F.R.S.E.

Assistant Lecturer.—W. M. Gardner.

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 Courseincludes instruction in chemistry, engineering, 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 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.

Lecturer on Metallurgy.—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers.—T. L. Bailey, Ph.D., C. A. Kohn, B.Sc., Ph.D., and S. B. Schryver, B.Sc., Ph.D.

Assistant.—H. H. Froysell.

The Session commences October 3rd.

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 nonmetallic 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.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3 10s.

Course C.—Organic Chemistry. Fee, £3 10s.

Course H.—Special Organic Subjects. Fee, £1.

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.

Courses 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 and Gas. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. Three terms. Fee, each course £1 10s.

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, Saitanry subjects, 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.

Additional metallurgy furnaces have been built, and a department for practical study of Electricity applied to Chemical Analysis has been added during the past year, and a large extension of the laboratories is in progress this year.

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.	21

Pharmaceutical Course, £11.

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). German. Or the Victoria Preliminary Course and Examination 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. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course E or D, Technological Chemistry, Course F, on Metallurgy. Chemical Laboratory, four pays 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.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1895, 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.

Evening Classes.

Classes will be held on Metallurgy and on Analysis of Gases.

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, M.A., 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.

The Session will commence on September 23rd, 1895.

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 a.m., and will commence on Wednesday, October 2nd. Fee, £3 10s. for the Session.

2. *Advanced Course.*—Inorganic Chemistry, Tuesdays 3 to 4 p.m., during the Session. Fee, £2; or for students taking Organic Chemistry, £1.

3. *Organic Chemistry.* — A Course of 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 Fridays 3 to 4 p.m., and will commence on Thursday, October 3rd. Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 8th.

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.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10.

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 two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; 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 of the University of Durham. 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 wil commence on Monday, September 23rd.

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.; B. Lean, B.A., D.Sc.; and W. A. Bone, B.Sc., Ph.D.

Lecturer in Dyeing and Printing.—Ernest Bentz.

Assistant Lecturer in Metallurgy.—Gilbert J. Fowler, M.Sc.

The Session begins on October 1, 1895, and ends on June 23, 1896.

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.

Chemistry Lecture Courses.

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.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the *College* Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; the John Buckley Scholarship; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture 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.

UNIVERSITY COLLEGE, NOTTINGHAM.

Departments of Chemistry and Metallurgy, and of Agriculture.

Professor of Chemistry.—Frank Clowes, D.Sc. Lond., F.I.C.

Demonstrators of Chemistry.—J. J. Sudborough, D.Sc., Ph.D., F.I.C., R. M. Caven, B.Sc., F.I.C., and G. Melland, B.Sc., A.R.S.M.

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 1895-96 will be as follows:—First Term, October 7th to December 21st; Second Term, January 20th to April 2nd; Third Term, April 20th to July 4th.

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. In his third year he attends a course on Advanced Organic Chemistry or Applied Chemistry. Fee for Day Lectures and Classes: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Advanced Organic Chemistry, 21s. per term.

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, 5s.

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 from 10 to 5, except on Saturday, when the hours are from 10 to 1, 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, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., six hours 30s., 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.

Pharmaceutical Students can at all times work in the Chemical Laboratory, taking work suitable for the preparation for the Minor Examinations. Special lectures will also be given in Chemistry and Materia Medica.

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. Tuesday and Friday from 10 to 11 a.m. Fee, £2 12s. 6d.

Second Year's Course.—Chemistry of Metals. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s. Chemical Philosophy, Thursday, 11 to 12. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on Electrolytic Analysis, and on the Chemistry of Coal Mining.

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.

Professor of Chemistry.—James Walker, Ph.D., D.Sc.

Assistant Lecturers.—F. J. Hambly, F.I.C., and J. R. Appleyard, F.C.S.

Lecture Assistant and Laboratory Steward.—J. Foggie, F.C.S.

The Winter Session begins on October 15th, and ends on March 21st. The Summer Session extends from May to July.

The First Year's Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. To supplement the Practical work of First Year's Laboratory Students a short course of Lectures on *Analytical Chemistry* will be offered. Special facilities are afforded to Research Students.

The Lectures and Laboratory Practice in Chemistry are recognised by the Medical Colleges of London and Edinburgh, as well as by the University of Edinburgh, for degrees in Science and Medicine. The Courses are suitable for the degrees of the University of London 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, as far as qualification in Chemistry is concerned.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor.—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

Lecturers.—L. Dobbin, Ph.D., and H. Marshall, D.Sc.

Assistants.—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. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. A class on Organic Chemistry is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Crystallography, by Dr. Marshall; fee, £2 2s.

In addition to the above, Lecture Courses are given by the Assistants on 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: Whole Day—Winter Session, £10 10s., Oct.-Dec., Jan.-March; or Summer Session, £5 5s. Half Day—Winter Session, £6 6s., Oct.-Dec., Jan.-March; or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. 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), Simple Quantitative Determinations (practical), and Gas Analysis (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.—John E. Mackenzie, Ph.D., B.Sc.

Demonstrators.—Andrew F. King and James B. Shand.

The Session begins October 8th, 1895.

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 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.

Professor of Chemistry.—G. G. Henderson, D.Sc., M.A.

Professor of Technical Chemistry.—E. J. Mills, D.Sc., F.R.S.

Assistants.—J. Hendrick, B.Sc., F.I.C., A. R. Ewing, Ph.D., and T. Gray, B.Sc., F.C.S.

Professor of Metallurgy.—A. Humboldt Sexton, F.C.S., F.R.S.E.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an 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.

Complete courses of instruction in Metallurgy and Mining will 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., F.R.S.

The Session begins on October 10th. A Competitive Examination, open to intending Students of Arts or Science, for about forty-five Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held in the beginning of October. About thirty of these Bursaries, are restricted to Men and thirteen to Women, seven of the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. Two are open to students of either sex. Two Scholarships of £100 each, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1895-96. A Hall of Residence is provided for Women Students. 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. Elementary Organic Chemistry is also included in the Course.

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 short Course of Laboratory Practice, intended to illustrate the principles of the science.

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, and of more advanced Inorganic 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 £10 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. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., D.Sc., F.R.S.E., &c.

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. Fee, £1.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

IV.—*Laboratory Pupils.*—The Chemical Laboratories 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).

Scholarships.—In addition to various Scholarships awarded in the Faculties of Arts and Medicine in which Chemistry forms a part of the examination, there are other valuable Scholarships awarded specially in connection with the schools of Chemistry and Physics.

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, 1895, and ends on June 8th, 1895. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) The General Course of Practical Chemistry, consisting of about forty Lectures of two hours each, begins on January 7th, 1895.—Fee for each Sessional Course, £3. (2) A Course for Pharmaceutical Students. (3) Special Courses.

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.

Demonstrator.—A. J. Walker.

The College Session is divided into three terms. The First Term extends from October 15 to December 21, the Second Term from January 6 to March 28, and the Third Term from April 13 to June 13.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. — 1. First year's Course, Arts and Engineering, embraces Inorganic and the Elements of General Chemistry. 2. First year's Course, Medicine, includes Inorganic and Elementary Organic Chemistry. 3. Third year's Course, Arts, is devoted to Advanced Organic Chemistry.

Laboratory Courses. — 1. Second year's Course, Arts and Engineering, consists of Exercises in Inorganic Qualitative Analysis. 2, Second year's Course, Medicine, includes Inorganic and Elementary Organic Qualitative Analysis and the Chemical Examination of Urine. 3. Third year's Course, Arts, embraces Quantitative Analysis and other experiments to suit the requirements of individual Students. 4. The Laboratories are also open to Students for work in other branches of Chemistry.

For Fees and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

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.—(Vacant).

The Session commences on Monday, October 1st, 1894, and ends on June 21st, 1895.

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.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net. — *City and Guilds Technical College, 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. 17th, and the Winter Session opens on Tuesday, October 1st. *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. 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 17th, 1895. *South London Technical Art School.*—Classes in Modelling, Design, Wood Engraving, Drawing and Painting, House Decoration, Machine Drawing and Design, Plaster-work, &c.

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, Physics, &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 September 24th, 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. J. Woodward, B.A., B.Sc. Lectures — Elementary, Tuesdays, 8.15 p.m.; Advanced, Thursdays, 6.15; Practical, Tuesdays, 6—8 p.m.; Thursdays, 7.30—9.30 p.m. *Organic Chemistry:* Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 6 to 7 p.m.; Practical, Wednesdays, 7 to 9 p.m.

The Central School of Chemistry and Pharmacy, 173, Marylebone Road, London.— Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c., and Mr. Lionel Cooper, F.C.S. Lectures are given on Chemistry, Physics, Botany, Materia Medica, Pharmacy, &c. Laboratory Instruction.

South London School of Pharmacy, Lim., 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 5, 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 guineas; afterwards 2½ guineas per month respectively, inclusive of all departments.

The Goldsmiths' Institute, New Cross, S.E.—Head of the Chemistry Department, Mr. A. G. Bloxam, F.I.C.; Assistants, Mr. H. C. L. Bloxam and Mr. Percy Tarver, A.R.C.S. Lectures and Practical Classes in General Chemistry, also in Chemistry applied to Leather Manufacture and Gas Manufacture, are held in the evenings from 7.30 to 10.0, and are open to both sexes.

People's Palace, Mile End Road, E. (Draper's Company's Institute).—Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; 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 23rd. A course for the London University B.Sc. Degree, including Honours, is now offered, and the Chemical Laboratory has been newly equipped. Every facility is offered to Students desiring to undertake Research work.

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 1st, 1894.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C. (Science Department of the Univ. Corr. Coll.).—The large Chemical, Biological, and Physical laboratories 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.

WESTMINSTER COLLEGE OF CHEMISTRY AND PHARMACY, Trinity Square, Borough, S.E. — Messrs. Wills and Wootton. Day and Evening Classes.

BRISTOL MEDICAL SCHOOL.—Mr. T. Coomber, F.C.S.

THE CLIFTON LABORATORY, Berkeley Square, Bristol.—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).—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.C.S. 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.—Theoretical and Practical Chemistry, Mr. E. Knecht, Ph.D., F.I.C., and Mr. J. Grant, F.I.C., F.C.S. Metallurgy, Mr. E. L. Rhead. At this important Municipal School, with an attendance of upwards of 3000 Students, there are organised Day Courses in Pure Chemistry, with applications to Dyeing, Bleaching, and Printing. In addition there are Evening Courses, not only in Pure Chemistry, but in Metallurgy, Iron and Steel Manufacture, Brewing, Oils, Colours and Varnishes, Oils and Fats, Soap Manufacture, Bleaching, Dyeing, and Printing, Coal Tar Products, Paper Manufacture, and Photography. The complete Syllabus (4d., by post 6d.) may be obtained on application to Mr. J. H. Reynolds, Director and Secretary, Princess Street, Manchester.

HIGHER GRADE SCHOOL, PATRICROFT.—Science and Art Day and Evening School, and Institute for Women. Demonstrator in Chemistry, Mr. R. J. B. Sanderson.

TECHNICAL INSTITUTE, Birley Street, Beswick.—Demonstrator in Chemistry, Mr. R. J. B. Sanderson.

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 Organic and Inorganic Chemistry, Metallurgy, Hygiene, Mathematics, &c., from October to May. Principal, W. Morgan, Ph.D., F.I.C.

ABERDEEN UNIVERSITY.—Prof. Japp.

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. Marshall.

CITY ANALYST'S LABORATORY AND CLASS ROOM, 138, Bath Street, Glasgow.—Messrs. Wallace and Clark.

GLASGOW UNIVERSITY.—Prof. J. Ferguson.

GLASGOW VETERINARY COLLEGE.—Professor Cooke.

ANDERSON'S COLLEGE, GLASGOW.—Mr. J. R. Watson.

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.

NEW GROUPING OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—I suppose some of your readers, before this letter can reach you, will have drawn your attention to the fact that the "New Grouping of the Elements," given by Thomsen in the current volume of *Zeitsch. f. Anorganische Chemie*, pp. 190—193, is identical with the one given by Carnelley (CHEMICAL NEWS, vol. liii.), and by him accredited to Bayley (*Phil. Mag.*, 5, xiii., p. 26). These latter authors divide the third group of Thomsen.

It seems strange that Thomsen should have overlooked the previous publication of the table.—I am, &c.,

F. P. VENABLE.

Department of Chemistry,
University of North Carolina,
August 17, 1895.

The Drug, Chemical, and Allied Trades Exhibition.—This useful Trade Exhibition will be opened at the Agricultural Hall, Islington, N., on Tuesday next, September 10th, and will be continued on the three following days. Exhibits have been received from most of the leading houses, and should form an interesting and varied display. The Manager will forward invitation tickets to any gentlemen connected with the trade who desire to attend. The Offices of the Exhibition are at 42, Bishopsgate Without, E.C.

The Manner of the Action of Dry Hydrochloric Acid upon Serpentine.—E. A. Schneider.—In this reaction there is a formation of water. A part of the water formed escapes with the hydrochloric acid; another portion is retained by the residual silicate. This residue, on treatment with dry hydrogen chloride, behaves like the original mol. of serpentine. Water is formed along with magnesium chloride. A part of the water formed is retained by the residual silicate, and there ensues an absorption of water. In the experiments of Clarke and Schneider the hydrogen chloride used was sufficiently dried to be regarded as "dry."—*Zeit. Anorg. Chem.*

THE CHEMICAL NEWS.

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BRITISH ASSOCIATION
FOR THE
ADVANCEMENT OF SCIENCE.

IPSWICH, 1895.

INAUGURAL ADDRESS OF THE PRESIDENT,
SIR DOUGLAS GALTON, K.C.B., D.C.L., F.R.S.

MY first duty is to convey to you, Mr. Mayor, and to the inhabitants of Ipswich, the thanks of the British Association for your hospitable invitation to hold our sixty-fifth meeting in your ancient town, and thus to recall the agreeable memories of the similar favour which your predecessors conferred on the Association forty-four years ago.

In the next place I feel it my duty to say a few words on the great loss which science has recently sustained—the death of the Right Hon. Thomas Henry Huxley. It is unnecessary for me to enlarge, in the presence of so many to whom his personality was known, upon his charm in social and domestic life; but upon the debt which the Association owes to him for the assistance which he rendered in the promotion of science I cannot well be silent. Huxley was pre-eminently qualified to assist in sweeping away the obstruction by dogmatic authority, which in the early days of the Association fettered progress in certain branches of science. For, whilst he was an eminent leader in biological research, his intellectual power, his original and intrepid mind, his vigorous and masculine English, made him a writer who explained the deepest subject with transparent clearness. And as a speaker his lucid and forcible style was adorned with ample and effective illustration in the lecture-room; and his energy and wealth of argument in a more public arena largely helped to win the battle of evolution, and to secure for us the right to discuss questions of religion and science without fear and without favour.

It may, I think, interest you to learn that Huxley first made the acquaintance of Tyndall at the meeting of the Association held in this town in 1851.

About forty-six years ago I first began to attend the meetings of the British Association, and I was elected one of your general secretaries about twenty-five years ago.

It is not unfitting, therefore, that I should recall to your minds the conditions under which science was pursued at the formation of the Association, as well as the very remarkable position which the Association has occupied in relation to science in this country.

Between the end of the sixteenth century and the early part of the present century several societies had been created to develop various branches of science. Some of these societies were established in London, and others in important provincial centres.

In 1831, in the absence of railways, communication between different parts of the country was slow and difficult. Science was therefore localised; and in addition to the universities in England, Scotland, and Ireland, the towns of Birmingham, Manchester, Plymouth, and York each maintained an important nucleus of scientific research.

ORIGIN OF THE BRITISH ASSOCIATION.

Under these social conditions the British Association was founded in September, 1831.

The general idea of its formation was derived from a migratory society which had been previously formed in Germany; but whilst the German society met for the special occasion on which it was summoned, and then dissolved, the basis of the British Association was continuity.

The objects of the founders of the British Association were enunciated in their earliest rules to be:—

"To give a stronger impulse and a more systematic direction to scientific inquiry; to promote the intercourse of those who cultivated science in different parts of the British Empire with one another, and with foreign philosophers; to obtain a more general attention to the objects of science, and a removal of any disadvantages of a public kind which impede its progress."

Thus the British Association for the Advancement of Science based its utility upon the opportunity it afforded for combination.

The first meeting of the Association was held at York with 353 members.

As an evidence of the want which the Association supplied, it may be mentioned that at the second meeting, which was held at Oxford, the number of members was 435. The third meeting, at Cambridge, numbered over 900 members; and at the meeting in Edinburgh in 1834 there were present 1298 members.

At its third meeting, which was held at Cambridge in 1833, the Association, through the influence it had already acquired, induced the Government to grant a sum of £500 for the reduction of the astronomical observations of Baily. And at the same meeting the General Committee commenced to appropriate to scientific research the surplus from the subscriptions of its members. The committees on each branch of science were desired "to select definite and important objects of science, which they may think most fit to be advanced by an application of the funds of the society, either in compensation for labour or in defraying the expense of apparatus, or otherwise, stating their reasons for their selection, and, when they may think proper, designating individuals to undertake the desired investigations."

The several proposals were submitted to the Committee of Recommendations, whose approval was necessary before they could be passed by the General Committee. The regulations then laid down still guide the Association in the distribution of its grants. At that early meeting the Association was enabled to apply £600 to these objects.

I have always wondered at the foresight of the framers of the constitution of the British Association, the most remarkable feature of which is the lightness of the tie which holds it together. It is not bound by any complex central organisation. It consists of a federation of Sections, whose youth and energy are yearly renewed by a succession of presidents and vice-presidents, whilst in each Section some continuity of action is secured by the less movable secretaries.

The governing body is the General Committee, the members of which are selected for their scientific work; but their controlling power is tempered by the law that all changes of rules, or of constitution, should be submitted to, and receive the approval of, the Committee of Recommendations. This committee may be described as an ideal Second Chamber. It consists of the most experienced members of the Association.

The administration of the Association in the interva between annual meetings is carried on by the Council, an executive body, whose duty it is to complete the work of the annual meeting (*a*) by the publication of its proceedings; (*b*) by giving effect to resolutions passed by the General Committee; (*c*) it also appoints the Local Committee and organises the *personnel* of each Section for the next meeting.

I believe that one of the secrets of the long-continued success and vitality of the British Association lies in this purely democratic constitution, combined with the compulsory careful consideration which must be given to suggested organic changes.

The Association is now in the sixty-fifth year of its existence. In its origin it invited the philosophical societies dispersed throughout Great Britain to unite in a co-operative union.

Within recent years it has endeavoured to consolidate that union.

At the present time almost all important local scientific societies scattered throughout the country, some sixty-six in number, are in correspondence with the Association. Their delegates hold annual conferences at our meetings. The Association has thus extended the sphere of its action: it places the members of the local societies engaged in scientific work in relation with each other, and brings them into co-operation with members of the Association and with others engaged in original investigations, and the papers which the individual societies publish annually are catalogued in our Report. Thus by degrees a national catalogue will be formed of the scientific work of these societies.

The Association has, moreover, shown that its scope is coterminous with the British Empire by holding one of its annual meetings at Montreal, and we are likely soon to hold a meeting in Toronto.

Condition of certain Sciences at the formation of the British Association.

The Association, at its first meeting, began its work by initiating a series of reports upon the then condition of the several sciences.

A rapid glance at some of these reports will not only show the enormous strides which have been made since 1831 in the investigation of facts to elucidate the laws of Nature, but it may afford a slight insight into the impediments offered to the progress of investigation by the mental condition of the community, which had been for so long satisfied to accept assumptions without undergoing the labour of testing their truth by ascertaining the real facts. This habit of mind may be illustrated by two instances selected from the early reports made to the Association. The first is afforded by the report made in 1832, by Mr. Lubbock, on "Tides."

This was a subject necessarily of importance to England as a dominant power at sea. But in England records of the tides had only recently been commenced at the dockyards of Woolwich, Sheerness, Portsmouth, and Plymouth, on the request of the Royal Society, and no information had been collected upon the tides on the coasts of Scotland and Ireland.

The British Associaton may feel pride in the fact that within three years of its inception, viz., by 1834, it had induced the Corporation of Liverpool to establish two tide gauges, and the Government to undertake tidal observations at 500 stations on the coasts of Britain.

Another cognate instance is exemplified by a paper read at the second meeting, in 1832, upon the State of Naval Architecture in Great Britain. The author contrasts the extreme perfection of the carpentry of the internal fittings of the vessels with the remarkable deficiency of mathematical theory in the adjustment of the external form of vessels, and suggests the benefit of the application of refined analysis to the various practical problems which ought to interest shipbuilders—problems of capacity, of displacement, of stowage, of velocity, of pitching and rolling, of masting, of the effects of sails, and of the resistance of fluids; and, moreover, suggests that large scale experiments should be made by Government, to afford the necessary data for calculation.

Indeed, when we consider how completely the whole habit of mind of the populations of the Western world has been changed, since the beginning of the century, from willing acceptance of authority as a rule of life to a universal spirit of inquiry and experimental investigation, is it not probable that this rapid change has arisen from society having been stirred to its foundations by the causes and consequences of the French Revolution?

One of the earliest practical results of this awakening in France was the conviction that the basis of scientific research lay in the accuracy of the standards by which observations could be compared; and the following principles were laid down as a basis for their measurements of length, weight, and capacity: viz. (1) that the unit of linear measure applied to matter in its three forms of extension, viz., length, breadth, and thickness, should be the standard of measures of length, surface, and solidity; (2) that the cubic contents of the linear measure in decimetres of pure water at the temperature of its greatest density should furnish at once the standard weight and the measure of capacity.* The metric system did not come into full operation in France till 1840, and it is now adopted by all countries on the continent of Europe except Russia.

The standards of length which were accessible in Great Britain at the formation of the Association were the Parliamentary standard yard lodged in the Houses of Parliament (which was destroyed in 1834 in the fire which burned the Houses of Parliament); the Royal Astronomical Society's standard; and the 10-foot bar of the Ordnance Survey.

The first two were assumed to afford exact measurements at a given temperature. The Ordnance bar was formed of two bars on the principle of a compensating pendulum, and afforded measurements independent of temperature. Standard bars were also disseminated throughout the country, in possession of the corporations of various towns.

The British Association early recognised the importance of uniformity in the record of scientific facts, as well as the necessity for an easy method of comparing standards, and for verifying differences between instruments and apparatus required by various observers pursuing similar lines of investigation. At its meeting at Edinburgh in 1834 it caused a comparison to be made between the standard bar at Aberdeen, constructed by Troughton, and the standard of the Royal Astronomical Society, and reported that the scale "was exceedingly well finished; it was about $\frac{1}{500}$th of an inch shorter than the 5-feet of the Royal Astronomical Society's scale, but it was evident that a great number of minute, yet important, circumstances have hitherto been neglected in the formation of such scales, without an attention to which they cannot be expected to accord with that degree of accuracy which the present state of science demands." Subsequently, at the meeting at Newcastle in 1863, the Association appointed a committee to report on the best means of providing for a uniformity of weights and measures with reference to the interests of science. This committee recommended the metric decimal system—a recommendation which has been endorsed by a committee of the House of Commons in the last session of Parliament.

British instrument-makers had been long conspicuous for accuracy of workmanship. Indeed, in the eighteenth century practical astronomy had been mainly in the hands of British observers; for although the mathematicians of France and other countries on the continent of Europe were occupying the foremost place in mathematical investigation, means of astronomical observation had been furnished almost exclusively by English artisans.

The sectors, quadrants, and circles of Ramsden, Bird, and Cary were inimitable by Continental workmen.

. . . . .

Lord Kelvin said in his Presidential Address at Edinburgh, "Nearly all the grandest discoveries of science have been but the rewards of accurate measurement and patient, long-continued labour in the sifting of numerical results." The discovery of argon, for which Lord Rayleigh and Professor Ramsay have been awarded the Hodgkin prize by the Smithsonian Institution, affords a remarkable illustration of the truth of this remark. In-

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* The litre is the volume of a kilogramme of pure water at its maximum density, and is slightly less than the litre was intended to be, viz., one cubic decimetre. The weight of a cubic decimetre of pure water is 1·00013 kilogrms.

deed, the provision of accurate standards not only of length, but of weight, capacity, temperature, force, and energy, are amongst the foundations of scientific investigation.

In 1842 the British Association obtained the opportunity of extending its usefulness in this direction.

In that year the Government gave up the Royal Observatory at Kew, and offered it to the Royal Society, who declined it. But the British Association accepted the charge. Their first object was to continue Sabine's valuable observations upon the vibrations of a pendulum in various gases, and to promote pendulum observations in various parts of the world. They subsequently extended it into an observatory for comparing and verifying the various instruments which recent discoveries in physical science had suggested for continuous meteorological and magnetic observations, for observations and experiments on atmospheric electricity, and for the study of solar physics.

This new departure afforded a means for ascertaining the advantages and disadvantages of the several varieties of scientific instruments; as well as for standardising and testing instruments, not only for instrument makers, but especially for observers by whom simultaneous observations were then being carried on in different parts of the world; and also for training observers proceeding abroad on scientific expeditions.

Its special object was to promote original research, and expenditure was not to be incurred on apparatus merely intended to exhibit the necessary consequences of known laws.

The rapid strides in electrical science had attracted attention to the measurement of electrical resistances, and in 1859 the British Association appointed a special committee to devise a standard. The standard of resistance proposed by that committee became the generally accepted standard, until the requirements of that advancing science led to the adoption of an international standard.

In 1866 the Meteorological Department of the Board of Trade entered into close relations with the Kew Observatory.

And in 1871 Mr. Gassiot transferred £10,000 upon trust to the Royal Society for the maintenance of the Kew Observatory, for the purpose of assisting in carrying on magnetical, meteorological, and other physical obvervations. The British Association thereupon, after having maintained this Observatory for nearly thirty years, at a total expenditure of about £12,000, handed the Observatory over to the Royal Society.

The "Transactions" of the British Association are a catalogue of its efforts in every branch of science, both to promote experimental research and to facilitate the application of the results to the practical uses of life.

But probably the marvellous development in science which has accompanied the life history of the Association will be best appreciated by a brief allusion to the condition of some of the branches of science in 1831 as compared with their present state.

GEOLOGICAL AND GEOGRAPHICAL SCIENCE.

Geology.

At the foundation of the Association geology was assuming a prominent position in science. The main features of English geology had been illustrated as far back as 1821, and, among the founders of the British Association, Murchison and Phillips, Buckland, Sedgwick, and Conybeare, Lyell and De la Beche, were occupied in investigating the data necessary for perfecting a geological chronology by the detailed observations of the various British deposits, and by their co-relation with the Continental strata. They were thus pieparing the way for those large generalisations which have raised geology to the rank of an inductive science.

In 1831 the Ordnance maps published for the southern counties had enabled the Government to recognise the importance of a geological survey by the appointment of Mr. De la Beche to affix geological colours to the maps of Devonshire and portions of Somerset, Dorset, and Cornwall; and in 1835 Lyell, Buckland, and Sedgwick induced the Government to establish the Geological Survey Department, not only for promoting geological science, but on account of its practical bearing on agriculture, mining, the making of roads, railways, and canals, and on other branches of national industry.

Geography.

The Ordnance Survey appears to have had its origin in a proposal of the French Government to make a joint measurement of an arc of the meridian. This proposal fell through at the outbreak of the Revolution; but the measurement of the base for that object was taken as a foundation for a national survey. In 1831, however, the Ordnance Survey had only published the 1-inch map for the southern portion of England, and the great triangulation of the kingdom was still incomplete.

In 1834 the British Association urged upon the Government that the advancement of various branches of science was greatly retarded by the want of an accurate map of the whole of the British Isles; and that, consequently, the engineer and the meteorologist, the agriculturist and the geologist, were each fettered in their scientific investigations by the absence of those accurate data which now lie ready to his hand for the measurement of length, of surface, and of altitude.

Yet the first decade of the British Association was coincident with a considerable development of geographical research. The Association was persistent in pressing on the Government the scientific importance of sending the expedition of Ross to the Antarctic and of Franklin to the Arctic regions. We may trust that we are approaching a solution of the geography of the North Pole; but the Antarctic regions still present a field for the researches of the meteorologist, the geologist, the biologist, and the magnetic observer, which the recent voyage of M. Borchgrevink leads us to hope may not long remain unexplored.

In the same decade the question of an alternative route to India by means of a communication between the Mediterranean and the Persian Gulf was also receiving attention, and in 1835 the Government employed Colonel Chesney to make a survey of the Euphrates valley in order to ascertain whether that river would enable a practicable route to be formed from Iskanderoon, or Tripoli, opposite Cyprus, to the Persian Gulf. His valuable surveys are not, however, on a sufficiently extensive scale to enable an opinion to be formed as to whether a navigable waterway through Asia Minor is physically practicable, or whether the cost of establishing it might not be prohibitive.

The advances of Russia in Central Asia have made it imperative to provide an easy, rapid, and alternative line of communication with our Eastern possessions, so as not to be dependent upon the Suez Canal in time of war. If a navigation cannot be established, a railway between the Mediterranean and the Persian Gulf has been shown by the recent investigations of Messrs. Hawkshaw and Hayter, following on those of others, to be perfectly practicable and easy of accomplishment; such an undertaking would not only be of strategical value, but it is believed it would be commercially remunerative.

Speke and Grant brought before the Association, at its meeting at Newcastle in 1863, their solution of the mystery of the Nile basin, which had puzzled geographers from the days of Herodotus; and the efforts of Livingstone and Stanley and others have opened out to us the interior of Africa. I cannot refrain here from expressing the deep regret which geologists and geographers, and indeed all who are interested in the progress of discovery, feel at the recent death of Joseph Thomson. His extensive, accurate, and trustworthy observations added much to our knowledge of Africa, and by his premature death we have lost one of its most competent explorers.

Chemical, Astronomical, and Physical Science.

Chemistry.

The report made to the Association on the state of the chemical sciences in 1832, says that the efforts of investigators were then being directed to determining with accuracy the true nature of the substances which compose the various products of the organic and inorganic kingdoms, and the exact ratios by weight which the different constituents of these substances bear to each other.

But since that day the science of chemistry has far extended its boundaries. The barrier has vanished which was supposed to separate the products of living organisms from the substances of which minerals consist, or which could be formed in the laboratory. The number of distinct carbon compounds obtainable from organisms has greatly increased; but it is small when compared with the number of such compounds which have been artificially formed. The methods of analysis have been perfected. The physical, and especially the optical, properties of the various forms of matter have been closely studied, and many fruitful generalisations have been made. The form in which these generalisations would now be stated may probably change, some, perhaps, by the overthrow or disuse of an ingenious guess at Nature's workings, but more by that change which is the ordinary growth of science—namely, inclusion in some simpler and more general view.

In these advances the chemist has called the spectroscope to his aid. Indeed, the existence of the British Association has been practically coterminous with the comparatively newly-developed science of spectrum analysis, for though Newton,[*] Wollaston, Fraunhofer, and Fox Talbot had worked at the subject long ago, it was not till Kirchhoff and Bunsen set a seal on the prior labours of Stokes, Angström, and Balfour Stewart that the spectra of terrestrial elements have been mapped out and grouped; that by its help new elements have been discovered, and that the idea has been suggested that the various orders of spectra of the same elements are due to the existence of the element in different molecular forms—allotropic or otherwise—at different temperatures.

But great as have been the advances of terrestrial chemistry through its assistance, the most stupendous advance which we owe to the spectroscope lies in the celestial direction.

Astronomy.

In the earlier part of this century, whilst the sidereal universe was accessible to investigators, many problems outside the solar system seemed to be unapproachable.

At the third meeting of the Association, at Cambridge, in 1833, Dr. Whewell said that astronomy is not only the queen of science, but the only perfect science, which was "in so elevated a state of flourishing maturity that all that remained was to determine with the extreme of accuracy the consequences of its rules by the profoundest combinations of mathematics; the magnitude of its data by the minutest scrupulousness of observation."

But in the previous year, viz., 1832, Airy, in his report to the Association on the progress of astronomy, had pointed out that the observations of the planet Uranus could not be united in one elliptic orbit; a remark which turned the attention of Adams to the discovery of Neptune. In his report on the position of optical science in 1832, Brewster suggested that with the assistance of adequate instruments "it would be possible to study the action of the elements of material bodies upon rays of artificial light, and thereby to discover the analogies between their affinities and those which produce the fixed lines in the spectra of the stars; and thus to study the effects of the combustions which light up the suns of other systems."

This idea has now been realised. All the stars which shine brightly enough to impress an image of the spectrum upon a photographic plate have been classified on a chemical basis. The close connection between stars and nebulæ has been demonstrated; and while on the one hand the modern science of thermodynamics has shown that the hypothesis of Kant and Laplace on stellar formation is no longer tenable, inquiry has indicated that the true explanation of stellar evolution is to be found in the gradual condensation of meteoritic particles, thus justifying the suggestions put forward long ago by Lord Kelvin and Professor Tait.

We now know that the spectra of many of the terrestrial elements in the chromosphere of the sun differ from those familiar to us in our laboratories. We begin to glean the fact that the chromospheric spectra are similar to those indicated by the absorption going on in the hottest stars, and Lockyer has not hesitated to affirm that these facts would indicate that in those localities we are in the presence of the actions of temperatures sufficiently high to break up our chemical elements into finer forms. Other students of these phenomena may not agree in this view, and possibly the discrepancies may be due to default in our terrestrial chemistry. Still, I would recall to you that Dr. Carpenter, in his Presidential Address at Brighton in 1872, almost censured the speculations of Frankland and Lockyer in 1868 for attributing a certain bright line in the spectrum of solar prominences (which was not identifiable with that of any known terrestrial source of light) to a hypothetical new substance which they proposed to call "helium," because "it had not received that verification which, in the case of Crookes's search for thallium, was afforded by the actual discovery of the new metal." Ramsay has now shown that this gas is present in dense minerals on earth; but we have now also learned from Lockyer that it and other associated gases are not only found with hydrogen in the solar chromosphere, but that these gases, with hydrogen, form a large percentage of the atmospheric constituents of some of the hottest stars in the heavens.

The spectroscope has also made us acquainted with the motions and even the velocities of those distant orbs which make up the sidereal universe. It has enabled us to determine that many stars, single to the eye, are really double, and many of the conditions of these strange systems have been revealed. The rate at which matter is moving in solar cyclones and winds is now familiar to us. And I may also add that quite recently this wonderful instrument has enabled Professor Keeler to verify Clerk-Maxwell's theory that the rings of Saturn consist of a marvellous company of separate moons—as it were, a cohort of courtiers revolving round their queen—with velocities proportioned to their distances from the planet.

Physics.

If we turn to the sciences which are included under physics, the progress has been equally marked.

In optical science, in 1831 the theory of emission as contrasted with the undulatory theory of light was still under discussion.

Young, who was the first to explain the phenomena due to the interference of the rays of light as a consequence of the theory of waves, and Fresnel, who showed the intensity of light for any relative position of the interference-waves, both had only recently passed away.

The investigations into the laws which regulate the conduction and radiation of heat, together with the doctrine of latent and of specific heat, and the relations of vapour to air, had all tended to the conception of a material heat, or caloric, communicated by an actual flow and emission.

It was not till 1834 that improved thermometrical appliances had enabled Forbes and Melloni to establish the polarisation of heat, and thus to lay the foundation of an

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[*] Joannes Marcus Marci, of Kronland in Bohemia, was the only predecessor of Newton who had any knowledge of the formation of a spectrum by a prism. He not only observed that the coloured rays diverged as they left the prism, but that a coloured ray did not change in colour after transmission through a prism. His book, "Thaumantias, liber de arcu cœlesti deque colorum apparentium natura," Prag, 1648, was, however, not known to Newton, and had no influence upon future discoveries.

undulatory theory for heat similar to that which was in progress of acceptation for light.

Whewell's report, in 1832, on magnetism and electricity shows that these branches of science were looked upon as cognate, and that the theory of two opposite electric fluids was generally accepted.

In magnetism, the investigations of Hansteen, Gauss, and Weber in Europe, and the observations made under the Imperial Academy of Russia over the vast extent of that empire, had established the existence of magnetic poles, and had shown that magnetic disturbances were simultaneous at all the stations of observation.

At their third meeting the Association urged the Government to establish magnetic and meteorological observatories in Great Britain and her colonies and dependencies in different parts of the earth, furnished with proper instruments, constructed on uniform principles, and with provisions for continued observations at those places.

In 1839 the British Association had a large share in inducing the Government to initiate the valuable series of experiments for determining the intensity, the declination, the dip, and the periodical variations of the magnetic needle, which were carried on for several years, at numerous selected stations over the surface of the globe, under the directions of Sabine and Lefroy.

In England systematic and regular observations are still made at Greenwich, Kew, and Stonyhurst. For some years past similar observations by both absolute and self-recording instruments have also been made at Falmouth —close to the home of Robert Were Fox, whose name is inseparably connected with the early history of terrestrial magnetism in this country—but under such great financial difficulties that the continuance of the work is seriously jeopardised. It is to be hoped that means may be forthcoming to carry it on. Cornishmen, indeed, could found no more fitting memorial of their distinguished countryman, John Couch Adams, than by suitably endowing the magnetic observatory in which he took so lively an interest.

Far more extended observation will be needed before we can hope to have an established theory as to the magnetism of the earth. We are without magnetic observations over a large part of the Southern Hemisphere. And Professor Rücker's recent investigations tell us that the earth seems as it were alive with magnetic forces, be they due to electric currents or to variations in the state of magnetised matter; that the disturbances affect not only the diurnal movement of the magnet, but that even the small part of the secular change which has been observed, and which has taken centuries to accomplish, is interfered with by some slower agency. And, what is more important, he tells us that none of these observations stand as yet upon a firm basis, because standard instruments have not been in accord; and much labour, beyond the power of individual effort, has hitherto been required to ascertain whether the relations between them are constant or variable.

In electricity, in 1831, just at the time when the British Association was founded, Faraday's splendid researches in electricity and magnetism at the Royal Institution had begun with his discovery of magneto-electric induction, his investigation of the laws of electro-chemical decomposition, and the mode of electrolytical action.

But, the practical application of our electrical knowledge was then limited to the use of lightning-conductors for buildings and ships. Indeed, it may be said that the applications of electricity to the use of man have grown up side by side with the British Association.

One of the first practical applications of Faraday's discoveries was in the deposition of metals and electroplating, which has developed into a large branch of national industry; and the dissociating effect of the electric arc, for the reduction of ores, and in other processes, is daily obtaining a wider extension.

But probably the application of electricity, which is tending to produce the greatest change in our mental, and even material condition, is the electric telegraph and its sister, the telephone. By their agency not only do we learn, almost at the time of their occurrence, the events which are happening in distant parts of the world, but they are establishing a community of thought and feeling between all the nations of the world which is influencing their attitude towards each other, and, we may hope, may tend to weld them more and more into one family.

The electric telegraph was introduced experimentally in Germany in 1833, two years after the formation of the Association. It was made a commercial success by Cooke and Wheatstone in England, whose first attempts at telegraphy were made on the line from Euston to Camden Town in 1837, and on the line from Paddington to West Drayton in 1838.

The submarine telegraph to America, conceived in 1856, became a practical reality in 1861 through the commercial energy of Cyrus Field and Pender, aided by the mechanical skill of Latimer Clark, Gooch, and others, and the scientific genius of Lord Kelvin. The knowledge of electricity gained by means of its application to the telegraph, largely assisted the extension of its utility in other directions.

The electric light gives, in its incandescent form, a very perfect hygienic light. Where rivers are at hand the electrical transmission of power will drive railway trains and factories economically, and might enable each artisan to convert his room into a workshop, and thus assist in restoring to the labouring man some of the individuality which the factory has tended to destroy.

In 1843 Joule described his experiments for determining the mechanical equivalent of heat. But it was not until the meeting at Oxford, in 1847, that he fully developed the law of the conservation of energy, which, in conjunction with Newton's law of the conservation of momentum, and Dalton's law of the conservation of chemical elements, constitutes a complete mechanical foundation for physical science.

Who, at the foundation of the Association, would have believed some far-seeing philosopher if he had foretold that the spectroscope would analyse the constituents of the sun and measure the motions of the stars; that we should liquefy air and utilise temperatures approaching to the absolute zero for experimental research; that, like the magician in the "Arabian Nights," we should annihilate distance by means of the electric telegraph and the telephone; that we should illuminate our largest buildings instantaneously, with the clearness of day, by means of the electric current; that by the electric transmission of power we should be able to utilise the Falls of Niagara to work factories at distant places; that we should extract metals from the crust of the earth by the same electrical agency to which, in some cases, their deposition has been attributed?

These discoveries and their applications have been brought to their present condition by the researches of a long line of scientific explorers, such as Dalton, Joule, Maxwell, Helmholtz, Herz, Kelvin, and Rayleigh, aided by vast strides made in mechanical skill. But what will our successors be discussing sixty years hence? How little do we yet know of the vibrations which communicate light and heat! Far as we have advanced in the application of electricity to the uses of life, we know but little even yet of its real nature. We are only on the threshold of the knowledge of molecular action, or of the constitution of the all-pervading æther. Newton, at the end of the seventeenth century, in his preface to the "Principia," says:—"I have deduced the motions of the planets by mathematical reasoning from forces; and I would that we could derive the other phenomena of Nature from mechanical principles by the same mode of reasoning. For many things move me, so that I somewhat suspect that all such may depend on certain forces by which the particles of bodies, through causes not yet known, are either urged towards each other according to regular figures, or are repelled and recede from each other; and these forces being unknown, philosophers have hitherto made their attempts on Nature in vain."

In 1848 Faraday remarked:—"How rapidly the knowledge of molecular forces grows upon us, and how strikingly every investigation tends to develop more and more their importance.

"A few years ago magnetism was an occult force, affecting only a few bodies; now it is found to influence all bodies, and to possess the most intimate relation with electricity, heat, chemical action, light, crystallisation; and through it the forces concerned in cohesion. We may feel encouraged to continuous labours, hoping to bring it into a bond of union with gravity itself."

But it is only within the last few years that we have begun to realise that electricity is closely connected with the vibrations which cause heat and light, and which seem to pervade all space—vibrations which may be termed the voice of the Creator calling to each atom and to each cell of protoplasm to fall into its ordained position, each, as it were, a musical note in the harmonious symphony which we call the universe.

Meteorology.

At the first meeting, in 1831, Prof. James D. Forbes was requested to draw up a report on the State of Meteorological Science, on the ground that this science is more in want than any other of that systematic direction which it is one great object of the Association to give.

Professor Forbes made his first report in 1832, and a subsequent report in 1840. The systematic records now kept, in various parts of the world, of barometric pressure, of solar heat, of the temperature and physical conditions of the atmosphere at various altitudes, of the heat of the ground at various depths, of the rainfall, of the prevalence of winds, and the gradual elucidation not only of the laws which regulate the movements of cyclones and storms, but of the influences which are exercised by the sun and by electricity and magnetism, not only upon atmospheric conditions, but upon health and vitality, are gradually approximating meteorology to the position of an exact science.

England took the lead in rainfall observations. Mr. J. G. Symons organised the British Rainfall System in 1860 with 178 observers, a system which until 1876 received the help of the British Association. Now Mr. Symons himself conducts it, assisted by more than 3000 observers, and these volunteers not only make the observations, but defray the expense of their reduction and publication. In foreign countries this work is done by Government officers at the public cost.

At the present time a very large number of rain-gauges are in daily use throughout the world. The British Islands have more than 3000, and India and the United States have nearly as many; France and Germany are not far behind; Australia probably has more—indeed, one colony alone, New South Wales, has more than 1100.

The storm warnings now issued under the excellent systematic organisation of the Meteorological Committee may be said to have had their origin in the terrible storm which broke over the Black Sea during the Crimean War, on November 27th, 1855. Leverrier traced the progress of that storm, and, seeing how its path could have been reported in advance by the electric telegraph, he proposed to establish observing stations which should report to the coasts the probability of the occurrence of a storm. Leverrier communicated with Airy, and the Government authorised Admiral FitzRoy to make tentative arrangements in this country. The idea was also adopted on the Continent, and now there are few civilised countries north or south of the Equator without a system of storm warming.*

BIOLOGICAL SCIENCE.

Botany.

The earliest Reports of the Association which bear on the biological sciences were those relating to botany.

In 1831 the controversy was yet unsettled between the advantages of the Linnean, or Artificial system, as contrasted with the Natural system of classification. Histology, morphology, and physiological botany, even if born, were in their early infancy.

Our records show that von Mohl noted cell division in 1835, the presence of chlorophyll corpuscles in 1837; and he first described protoplasm in 1846.

Vast as have been the advances of physiological botany since that time, much of its fundamental principles remain to be worked out, and I trust that the establishment, for the first time, of a permanent Section for botany at the present meeting will lead the Association to take a more prominent part than it has hitherto done in the further development of this branch of biological science.

Animal Physiology.

In 1831 Cuvier, who during the previous generation had, by the collation of facts followed by careful inductive reasoning, established the plan on which each animal is constructed, was approaching the termination of his long and useful life. He died in 1832; but in 1831 Richard Owen was just commencing his anatomical investigations and his brilliant contributions to palæontology.

The impulse which their labours gave to biological science was reflected in numerous reports and communications, by Owen and others, throughout the early decades of the British Association, until Darwin propounded a theory of evolution which commanded the general assent of the scientific world. For this theory was not absolutely new. But just as Cuvier had shown that each bone in the fabric of an animal affords a clue to the shape and structure of the animal, so Darwin brought harmony into scattered facts, and led us to perceive that the moulding hand of the Creator may have evolved the complicated structures of the organic world from one or more primeval cells.

Richard Owen did not accept Darwin's theory of evolution, and a large section of the public contested it. I well remember the storm it produced—a storm of praise by my geological colleagues, who accepted the result of investigated facts; a storm of indignation, such as that which would have burned Galileo at the stake, from those who were not yet prepared to question the old authorities; but they diminish daily.

We are, however, as yet only on the threshold of the doctrine of evolution. Does not each fresh investigation, even into the embryonic stage of the simpler forms of life, suggest fresh problems?

Anthropology.

The impulse given by Darwin has been fruitful in leading others to consider whether the same principle of evolution may not have governed the moral as well as the material progress of the human race. . . . Evolution, as Sir William Flower said, is the message which biology has sent to help us on with some of the problems of human life, and Francis Galton urges that man, the foremost outcome of the awful mystery of evolution, should realise that he has the power of shaping the course of future humanity by using his intelligence to discover and expedite the changes which are necessary to adapt circumstances to man, and man to circumstances.

In considering the evolution of the human race, the science of preventive medicine may afford us some indication of the direction in which to seek for social improvement. One of the earliest steps towards establishing that

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* It has often been supposed that Leverrier was also the first to issue a daily weather map, but that was not the case, for in the Great Exhibition of 1851 the Electric Telegraph Company sold daily weather maps, copies of which are still in existence, and the data for them were, it is believed, obtained by Mr. James Glaisher, F.R.S., at that time Superintendent of the Meteorological Department at Greenwich.

science upon a secure basis was taken in 1835 by the British Association, who urged upon the Government the necessity of establishing registers of mortality showing the cause of death "on one uniform plan in all parts of the King's dominions, as the only means by which general laws touching the influence of causes of disease and death could be satisfactorily deduced." The general registration of births and deaths was commenced in 1838. But a mere record of death and its proximate cause is insufficient. Preventive medicine requires a knowledge of the details of the previous conditions of life and of occupation. Moreover, death is not our only or most dangerous enemy, and the main object of preventive medicine is to ward off disease. Disease of body lowers our useful energy. Disease of body or of mind may stamp its curse on succeeding generations.

The anthropometric laboratory affords to the student of anthropology a means of analysing the causes of weakness, not only in bodily, but also in mental life.

Mental actions are indicated by movements and their results. Such signs are capable of record, and modern physiology has shown that bodily movements correspond to action in nerve-centres, as surely as the motions of the telegraph-indicator express the movements of the operator's hands in the distant office.

Thus there is a relation between a defective status in brain power and defects in the proportioning of the body. Defects in physiognomical details, too finely graded to be measured with instruments, may be appreciated with accuracy by the senses of the observer; and the records show that these defects are, in a large degree, associated with a brain status lower than the average in mental power.

A report presented by one of your committees gives the results of observations made on 100,000 school children examined individually in order to determine their mental and physical condition for the purpose of classification. This shows that about 16 per 1000 of the elementary school population appear to be so far defective in their bodily or brain condition as to need special training to enable them to undertake the duties of life, and to keep them from pauperism or crime.

Many of our feeble-minded children, and much disease and vice, are the outcome of inherited proclivities. Francis Galton has shown us that types of criminals which have been bred true to their kind are one of the saddest disfigurements of modern civilisation; and he says that few deserve better of their country than those who determine to lead celibate lives through a reasonable conviction that their issue would probably be less fitted than the generality to play their part as citizens.

These considerations point to the importance of preventing those suffering from transmissible disease, or the criminal, or the lunatic, from adding fresh sufferers to the teeming misery in our large towns. And in any case, knowing as we do the influence of environment on the development of individuals, they point to the necessity of removing those who are born with feeble minds, or under conditions of moral danger, from surrounding deteriorating influences.

These are problems which materially affect the progress of the human race, and we may feel sure that, as we gradually approach their solution, we shall more certainly realise that the theory of evolution, which the genius of Darwin impressed on this century, is but the first step on a biological ladder which may possibly eventually lead us to understand how in the drama of creation man has been evolved as the highest work of the Creator.

Bacteriology.

The sciences of medicine and surgery were largely represented in the earlier meetings of the Association, before the creation of the British Medical Association afforded a field for their more intimate discussion. The close connection between the different branches of science is causing a revival in our proceedings of discussions on some of the highest medical problems, especially those relating to the spread of infectious and epidemic disease.

It is interesting to contrast the opinion prevalent at the foundation of the Association with the present position of the question,

A report to the Association in 1834, by Professor Henry, on contagion, says:—

"The notion that contagious emanations are at all connected with the diffusion of animalculæ through the atmosphere is at variance with all that is known of the diffusion of volatile contagion."

Whilst it had long been known that filthy conditions in air, earth, and water fostered fever, cholera, and many other forms of disease, and that the disease ceased to spread on the removal of these conditions, yet the reason for their propagation or diminution remained under a veil.

Leeuwenhoek in 1680 described the yeast-cells, but Schwann in 1837 first showed clearly that fermentation was due the activity of the yeast-cells; and, although vague ideas of fermentation had been current during the past century, he laid the foundation of our exact knowledge of the nature of the action of ferments, both organised and unorganised. It was not until 1860, after the prize of the Academy of Sciences had been awarded to Pasteur for his essay against the theory of spontaneous generation, that his investigations into the action of ferments* enabled him to show that the effects of the yeast-cell are indissolubly bound up with the activities of the cell as a living organism, and that certain diseases, at least, are due to the action of ferments in the living being. In 1865 he showed that the disease of silk worms, which was then undermining the silk industry in France, could be successfully combated. His further researches into anthrax, fowl cholera, swine fever, rabies, and other diseases proved the theory that those diseases are connected in some way with the introduction of a microbe into the body of an animal; that the virulence of the poison can be diminished by cultivating the microbes in an appropriate manner; and that when the virulence has been thus diminished their inoculation will afford a protection against the disease.

Meanwhile it had often been observed in hospital practice that a patient with a simple-fractured limb was easily cured, whilst a patient with a compound fracture often died from the wound. Lister was thence led, in 1865, to adopt his antiseptic treatment, by which the wound is protected from hostile microbes.

These investigations, followed by the discovery of the existence of a multitude of micro-organisms and the recognition of some of them—such as the bacillus of tubercle and the comma bacillus of cholera—as essential factors of disease; and by the elaboration by Koch and others of methods by which the several organisms might be isolated, cultivated, and their histories studied, have gradually built up the science of bacteriology. Amongst later developments are the discovery of various so-called antitoxins, such as those of diphtheria and tetanus, and the utilisation of these for the cure of disease. Lister's treatment formed a landmark in the science of surgery, and enabled our surgeons to perform operations never before dreamed of; whilst later discoveries are tending to place the practice of medicine on a firm scientific basis. And the science of bacteriology is leading us to recur to stringent rules for the isolation of infectious disease, and to the disinfection (by superheated steam) of materials which have been in contact with the sufferer.

These microbes, whether friendly or hostile, are all capable of multiplying at an enormous rate under favour-

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* In speaking of ferments one must bear in mind that there are two classes of ferments; one, living beings, such as yeast—"organised" ferments, as they are sometimes called—the other the products of living beings themselves, such as pepsin, &c.,—"unorganised" ferments. Pasteur worked with the former, very little with the latter.

able conditions. They are found in the air, in water, in the soil; but, fortunately, the presence of one species appears to be detrimental to other species, and sunshine, or even light from the sky, is prejudicial to most of them. Our bodies, when in health, appear to be furnished with special means of resisting attacks, and, so far as regards their influence in causing disease, the success of the attack of a pathogenic organism upon an individual depends, as a rule, in part at least, upon the power of resistance of the individual.

But notwithstanding our knowledge of the danger arising from a state of low health in individuals, and of the universal prevalence of these micro-organisms, how careless we are in guarding the health conditions of every-day life! We have ascertained that pathogenic organisms pervade the air. Why, therefore, do we allow our meat, our fish, our vegetables, our easily-contaminated milk, to be exposed to their inroads, often in the foulest localities? We have ascertained that they pervade the water we drink, yet we allow foul water from our dwellings, our pig-sties, our farmyards, to pass into ditches without previous clarification, whence it flows into our streams and pollutes our rivers. We know the conditions of occupation which foster ill-health. Why, whilst we remove outside sources of impure air, do we permit the occupation of foul and unhealthy dwellings?

The study of bacteriology has shown us that although some of these organisms may be the accompaniments of disease, yet we owe it to the operation of others that the refuse caused by the cessation of animal and vegetable life is re-converted into food for fresh generations of plants and animals.

These considerations have formed a point of meeting where the biologist, the chemist, the physicist, and the statistician unite with the sanitary engineer in the application of the science of preventive medicine.

ENGINEERING.

Sewage Purification.

The early reports to the Association show that the laws of hydrostatics, hydrodynamics, and hydraulics, necessary to the supply and removal of water through pipes and conduits, had long been investigated by the mathematician. But the modern sanitary engineer has been driven by the needs of an increasing population to call in the chemist and the biologist to help him to provide pure water and pure air.

The purification and the utilisation of sewage occupied the attention of the British Association as early as 1864, and between 1869 and 1876 a committee of the Association made a series of valuable reports on the subject. The direct application of sewage to land, though effective as a means of purification, entailed difficulties in thickly settled districts, owing to the extent of land required. . . .

It was not till the chemist called to his aid the biologist that a scientific system of sewage purification was evolved. The valuable experiments made in recent years by the State Board of Health in Massachusetts have more clearly explained to us how by this system we may utilise micro-organisms to convert organic impurity in sewage into food fitted for higher forms of life.

To effect this we require, in the first place, a filter about 5 feet thick of sand and gravel, or, indeed, of any material which affords numerous surfaces or open pores. Secondly, that after a volume of sewage has passed through the filter, an interval of time be allowed, in which the air necessary to support the life of the micro-organisms is enabled to enter the pores of the filter. Thus this system is dependent upon oxygen and time. Under such conditions the organisms necessary for purification are sure to establish themselves in the filter before it has been long in use. Temperature is a secondary consideration.

Imperfect purification can invariably be traced either to a lack of oxygen in the pores of the filter, or to the sewage passing through so quickly that there is not sufficient time for the necessary processes to take place. And the power of any material to purify either sewage or water depends almost entirely upon its ability to hold a sufficient proportion of either sewage or water in contact with a proper amount of air.

Smoke Abatement.

Whilst the sanitary engineer has done much to improve the surface conditions of our towns, to furnish clean water, and to remove our sewage, he has as yet done little to purify town air. Fog is caused by the floating particles of matter in the air becoming weighted with aqueous vapour; some particles, such as salts of ammonia or chloride of sodium, have a greater affinity for moisture than others. You will suffer from fog so long as you keep refuse stored in your towns to furnish ammonia, or so long as you allow your street surfaces to supply dust, of which much consists of powdered horse manure, or so long as you send the products of combustion into the atmosphere. Therefore, when you have adopted mechanical traction for your vehicles in towns you may largely reduce one cause of fog. And if you diminish your black smoke, you will diminish black fogs.

In manufactories you may prevent smoke either by care in firing, by using smokeless coal, or by washing the soot out of the products of consumption in its passage along the flue leading to the main chimney-shaft.

The black smoke from your kitchen may be avoided by the use of coke or of gas. But so long as we retain the hygienic arrangement of the open fire in our living rooms I despair of finding a fireplace, however well constructed, which will not be used in such a manner as to cause smoke, unless, indeed, the chimneys were reversed and the fumes drawn into some central shaft, where they might be washed before being passed into the atmosphere.

Electricity as a warming and cooking agent would be convenient, cleanly, and economical when generated by water power, or possibly wind power, but it is at present too dear when it has to be generated by means of coal. I can conceive, however, that our descendants may learn so to utilise electricity that they in some future century may be enabled by its means to avoid the smoke in their towns.

Mechanical Engineering.

In other branches of civil and mechanical engineering the reports in 1831 and 1832, on the state of this science, show that the theoretical and practical knowledge of the strength of timber had obtained considerable development; but in 1830, before the introduction of railways, cast-iron had been sparingly used in arched bridges for spans of from 160 to 200 feet, and wrought-iron had only been applied to large-span iron bridges on the suspension principle, the most notable instance of which was the Menai Suspension Bridge, by Telford. Indeed, whilst the strength of timber had been patiently investigated by engineers, the best form for the use of iron girders and struts was only beginning to attract attention, and the earlier volumes of our *Proceedings* contained numerous records of the researches of Eaton Hodgkinson, Barlow, Rennie, and others. It was not until twenty years later that Robert Stephenson and William Fairbairn erected the tubular bridge at Menai, followed by the more scientific bridge erected by Brunel at Saltash. These have now been entirely eclipsed by the skill with which the estuary of the Forth has been bridged with a span of 1700 feet, by Sir John Fowler and Sir Benjamin Baker.

The development of the iron industry is due to the association of the chemist with the engineer. The introduction of the hot blast by Neilson, in 1829, in the manufacture of cast-iron, had effected a large saving of fuel. But the chemical conditions which affect the strength and other qualities of iron, and its combinations with carbon, silicon, phosphorus, and other substances, had at that time scarcely been investigated.

In 1856 Bessemer brought before the British Association, at Cheltenham, his brilliant discovery for making steel direct from the blast furnace, by which he dispensed with the laborious process of first removing the carbon from pig-iron by puddling, and then adding by cementation the required proportion of carbon to make steel. This discovery, followed by Siemens's regenerative furnace, by Whitworth's compressed steel, and by the use of alloys, and by other improvements too numerous to mention here, have revolutionised the conditions under which metals are applied to engineering purposes.

Indeed, few questions are of greater interest, or possess more industrial importance, than those connected with metallic alloys. This is especially true of those alloys which contain the rarer metals; and the extraordinary effects of small quantities of chromium, nickel, tungsten, and titanium, on certain varieties of steel, have exerted profound influence on the manufacture of projectiles and on the construction of our armoured ships.

Of late years, investigations on the properties and structure of alloys have been numerous, and among the more noteworthy researches may be mentioned those of Dewar and Fleming on the distinctive behaviour, as regards the thermo-electric powers and electrical resistance, of metals and alloys at the very low temperatures which may be obtained by the use of liquid air.

Professor Roberts-Austen, on the other hand, has carefully studied the behaviour of alloys at very high temperatures, and by employing his delicate pyrometer has obtained photographic curves which afford additional evidence as to the existence of allotropic modifications of metals, and which have materially strengthened the view that alloys are closely analogous to saline solutions. In this connection it may be stated that the very accurate work of Heycock and Neville, on the lowering of the solidifying points of molten metals, which is caused by the presence of other metals, affords a valuable contribution to our knowledge.

Professor Roberts-Austen has, moreover, shown that the effect of any one constituent of an alloy upon the properties of the principal metal has a direct relation to the atomic volumes, and that it is consequently possible to foretell, in a great measure, the effect of any given combination.

A new branch of investigation, which deals with the micro-structure of metals and alloys, is rapidly assuming much importance. It was instituted by Sorby in a communication which he made to the British Association in 1864, and its development is due to many patient workers, among whom M. Osmond occupies a prominent place.

Metallurgical science has brought aluminium into use by cheapening the process of its extraction; and if by means of the wasted forces in our rivers, or possibly of the wind, the extraction be still further cheapened by the aid of electricity, we may not only utilise the metal or its alloys in increasing the spans of our bridges, and in affording strength and lightness in the construction of our ships, but we may hope to obtain a material which may render practicable the dreams of Icarus and of Maxim, and for purposes of rapid transit enable us to navigate the air.

Long before 1831 the steam-engine had been largely used on rivers and lakes, and for short sea passages, although the first Atlantic steam-service was not established till 1838.

As early as 1820 the steam-engine had been applied by Gurney, Hancock, and others to road traction. The absurd impediments placed in their way by road trustees, which, indeed, are still enforced, checked any progress. But the question of mechanical traction on ordinary roads was practically shelved in 1830, at the time of the formation of the British Association, when the locomotive engine was combined with a tubular boiler and an iron road on the Liverpool and Manchester Railway.

Great, however, as was the advance made by the locomotive engine of Robert Stephenson, these earlier engines were only toys compared with the compound engines of to-day which are used for railways, for ships, or for the manufacture of electricity. Indeed, it may be said that the study of the laws of heat, which have led to the introduction of various forms of motive power, are gradually revolutionising all our habits of life.

The improvements in the production of iron, combined with the developed steam-engine, have completely altered the conditions of our commercial intercourse on land; whilst the changes caused by the effects of these improvements in ship-building, and on the ocean carrying trade, have been, if anything, still more marked. . . .

The use of iron favours the construction of ships of a large size, of forms which afford small resistance to the water, and with compartments which make the ships practically unsinkable in heavy seas, or by collision. Their size, the economy with which they are propelled, and the certainty of their arrival cheapens the cost of transport.

The steam-engine, by compressing air, gives us control over the temperature of cool chambers. In these, not only fresh meat, but the delicate produce of the Antipodes, is brought across the ocean to our doors without deterioration.

Whilst railways have done much to alter the social conditions of each individual nation, the application of iron and steam to our ships is revolutionising the international commercial conditions of the world; and it is gradually changing the course of our agriculture, as well as of our domestic life.

But great as have been the developments of science in promoting the commerce of the world, science is asserting its supremacy even to a greater extent in every department of war. And perhaps this application of science affords at a glance, better than almost any other, a convenient illustration of the assistance which the chemical, physical, and electrical sciences are affording to the engineer.

The reception of warlike stores is not now left to the uncertain judgment of "practical men," but is confided to officers who have received a special training in chemical analysis, and in the application of physical and electrical science to the tests by which the qualities of explosives, of guns, and of projectiles can be ascertained.

For instance, take explosives. Till quite recently black and brown powders alone were used, the former as old as civilisation, the latter but a small modern improvement adapted to the increased size of guns. But now the whole family of nitro-explosives are rapidly superseding the old powder. These are the direct outcome of chemical knowledge; they are not mere chance inventions, for every improvement is based on chemical theories, and not on random experiment.

The construction of guns is no longer a haphazard operation. In spite of the enormous forces to be controlled and the sudden violence of their action, the researches of the mathematician have enabled the just proportions to be determined with accuracy; the labours of the physicist have revealed the internal conditions of the materials employed, and the best means of their favourable employment. Take, for example, Longridge's coiled-wire system, in which each successive layer of which the gun is formed receives the exact proportion of tension which enables all the layers to act in unison. The chemist has rendered it clear that even the smallest quantities of certain ingredients are of supreme importance in affecting the tenacity and trustworthiness of the materials.

The treatment of steel to adapt it to the vast range of duties it has to perform is thus the outcome of patient research. And the use of the metals—manganese, chromium, nickel, molybdenum—as alloys with iron has resulted in the production of steels possessing varied and extraordinary properties. The steel required to resist the conjugate stresses developed, lightning-fashion, in a gun necessitates qualities that would not be suitable in the projectile which that gun hurls with a velocity of some

2500 feet per second against the armoured side of a ship. The armour, again, has to combine extreme superficial hardness with great toughness, and during the last few years these qualities are sought to be attained by the application of the cementation process for adding carbon to one face of the plate, and hardening that face alone by rapid refrigeration.

The introduction of quick-firing guns from 0·303 (*i.e.*, about one-third) of an inch to 6-inch calibre has rendered necessary the production of metal cartridge-cases of complex forms drawn cold out of solid blocks or plate of the material; this again has taxed the ingenuity of the mechanic in the device of machinery, and of the metallurgist in producing a metal possessed of the necessary ductility and toughness. The cases have to stand a pressure at the moment of firing of as much as twenty-five tons to the square inch—a pressure which exceeds the ordinary elastic limits of the steel of which the gun itself is composed.

There is nothing more wonderful in practical mechanics than the closing of the breech openings of guns, for not only must they be gas-tight at these tremendous pressures, but the mechanism must be such that one man by a single continuous movement shall be able to open or close the breech of the largest gun in some ten or fifteen seconds.

The perfect knowledge of the recoil of guns has enabled the reaction of the discharge to be utilised in compressing air or springs by which guns can be raised from concealed positions in order to deliver their fire, and then made to disappear again for loading; or the same force has been used to run up the guns automatically immediately after firing, or, as in the case of the Maxim gun, to deliver in the same way a continuous stream of bullets at the rate of ten in one second.

In the manufacture of shot and shell cast-iron has been almost superseded by cast and wrought steel, though the hardened Palliser projectiles still hold their place. The forged-steel projectiles are produced by methods very similar to those used in the manufacture of metal cartridge-cases, though the process is carried on at a red heat and by machines much more powerful.

In every department concerned in the production of war-like stores electricity is playing a more and more important part. It has enabled the passage of a shot to be followed from its seat in the gun to its destination.

In the gun, by means of electrical contacts arranged in the bore, a time curve of the passage of the shot can be determined.

From this the mathematician constructs the velocity-curve, and from this, again, the pressures producing the velocity are estimated, and used to check the same indications obtained by other means. The velocity of the shot after it has left the gun is easily ascertained by the Boulangé apparatus.

Electricity and photography have been laid under contribution for obtaining records of the flight of projectiles and the effects of explosions at the moment of their occurrence. Many of you will recollect Mr. Vernon Boys' marvellous photographs showing the progress of the shot driving before it waves of air in its course.

Electricity and photography also record the properties of metals and their alloys as determined by curves of cooling.

The readiness with which electrical energy can be converted into heat or light has been taken advantage of for the firing of guns, which in their turn can, by the same agency, be laid on the object by means of range-finders placed at a distance and in advantageous and safe positions; while the electric light is utilised to illumine the sights at night, as well as to search out the objects of attack.

The compact nature of the glow-lamp, the brightness of the light, the circumstance that the light is not due to combustion, and therefore independent of air, facilitates the examination of the bore of guns, the insides of shells, and other similar uses—just as it is used by a doctor to examine the throat of a patient.

(To be continued).

A REFORM IN CHEMICAL, PHYSICAL, AND TECHNICAL CALCULATIONS.

By C. J. HANSSEN, C.E.

(Continued from p. 103).

The external caloric work of steam, which is overcoming atmospheric or other outer resistance, and is able to do mechanical or dynamic work, is, pro 1 cbm. steam pro 1 atmosphere pressure, at any temperature = $24\frac{3}{8}$ calors. pro 1 kg. steam $= \frac{\text{absolute temperature}}{9}$; consequently—

$$\text{At } 219\tfrac{3}{8}^\circ \text{ absol.} \ldots\ldots\ldots = \frac{219\frac{3}{8}^\circ}{9} = 24\tfrac{3}{8} \text{ calors.}$$

$$\text{At } 273^\circ \quad ,, \quad \ldots\ldots\ldots = \frac{273^\circ}{9} = 30\tfrac{1}{3} \quad ,,$$

$$\text{At } 373^\circ \quad ,, \quad (1 \text{ atmosph.}) = \frac{373^\circ}{9} = 41\tfrac{4}{9} \quad ,,$$

$$\text{At } 454^\circ \quad ,, \quad (10 \text{ atmosph.}) = \frac{454^\circ}{9} = 50\tfrac{4}{9} \quad ,,$$

The product of absolute pressure × volume per kg. (V × P) increases in direct ratio to the absolute temperature of steam, as shown by the diagonal straight V P line in the diagram.

Combustion.

When a substance is burnt we feel the heat produced, and see flames and light emit from the burning object, and we have been thus led to imagine that it is the visible object only which burns, and the heat developed in the process of burning we commonly consider to be the quantity of heat which the burning substance—for instance, 1 kg. of coal—is able to produce; we may, however, just as well reverse the case, and consider the heat developed in the process of combustion as produced by combining a certain quantity of *oxygen* with the burning substance, and measure the heat produced by the quantity of oxygen which combines with the burning substance.

All substances combine with other substances in simple definite proportions, and this rule also holds good in the chemical process termed combustion; we may therefore be sure that 1 kg. of oxygen, when combining with any other substance, *always will produce the same quantity of heat*, just as well as 1 kg. of carbon, if in combustion or by any other chemical process combined with oxygen, always produces a certain and definite quantity of heat. If experience in some cases seems to contradict this rule, and apparently gives different results, this can only be caused by imperfections in the method and apparatus used in the research, and such anomalies will by-and-bye be found out and corrected.

Of all substances at our disposal, capable of producing heat, carbon, hydrogen, and oxygen are the most generally applicable; and a correct determination of the value of their compounds as producers of heat will therefore be of the highest importance for science and industry, but as yet the chief authorities disagree on this subject.

The quantity of heat produced by combustion of 1 kg. of hydrogen of 273° absolute, with 8 kg. of oxygen of the same temperature, is found by—

		Calors.	
Andrews	=	33881	The vapour produced condensed to liquid water of 0° N = 273° absolute.
Humphrys	=	34722	
Favre and Silbermann	=	34462	
Dulong	=	34742	
Thomsen	=	34181	
Fischer	=	34384	
Berthelot	=	34600	

and the quantity of heat produced by combustion of 1 kg. of carbon monoxide with oxygen is found by—

Favre and Silbermann ..	= 2403 calors.
Dulong	= 2489 „
Fischer	= 2440 „
Ferguson Bell	= 2444 „
Humphrys	= 2489 „

As not two of these agree, it seems evident that all are more or less erroneous.

The author has shown (Chemical News, lxxii., p. 8) that 1 kg. hydrogen of 0° N (273° N absol.) burnt with 8 kg. oxygen, and the product of combustion condensed to the initial temperature of the components, produces 34679·70 calors., which in all following calculations is rounded off to 34680 calors.

This figure, being the mean of Messrs. Humphrys, Favre and Silbermann's, Dulong, and Berthelot's determinations, the author considers to be a correct standard, from which the heating power of other substances may be calculated, and consequently we find that—

1 cbm. of *hydrogen* of atmospheric density and 0° N, which weighs $\frac{5}{56}$ kg., will produce $34680 \times \frac{5}{56} = 3096\frac{3}{7}$ calors; that—

1 kg. of *oxygen* will produce $\frac{34680}{8} = 4335$ calors., and—

1 cbm. of *oxygen* of atm. density and 0° N $- 4335 \times \frac{10}{7} = 6192\frac{6}{7}$ calors., and 1 litre oxygen $\frac{6192\frac{6}{7}}{1000} = 6\frac{27}{140} = \frac{867}{140}$ calors; and further—

1 kg, of *aëriform carbon*, burning with $1\frac{1}{3}$ kg. oxygen, will produce $4335 \times 1\frac{1}{3} = 5780$ calors., forming $2\frac{1}{3}$ kg. CO.

1 cbm. of *aeriform carbon* (atmospheric density and 0° N), burnt with 1 cbm. oxygen of equal density and temperature, will produce $6192\frac{6}{7}$ cal. × 1 cbm. O $= 6192\frac{6}{7}$ calors., forming 2 cbm. CO.

1 kg. of *aeriform carbon*, burning with $2\frac{2}{3}$ kg. oxygen, will produce $4335 \times 2\frac{2}{3} = 11560$ calors., forming $3\frac{2}{3}$ kg. CO_2; and—

1 cbm *aeriform carbon*, burning with 2 cbm. oxygen, will produce $6192\frac{6}{7}$ cal. $\times 2 = 12385\frac{5}{7}$ calors., forming 2 cbm. CO_2.

1 kg. of *carbon monoxide*, which contains $\frac{3}{7}$ kg.. of aëriform carbon, burning with $\frac{4}{7}$ kg. oxygen, will produce $\frac{4}{7} \times 4535$ cal. $= 2477\frac{1}{7}$ calors., forming $1\frac{4}{7}$ kg. CO_2; and—

1 cbm. of *carbon monoxide*, which contains $\frac{1}{2}$ cbm. of aëriform carbon, burning with $\frac{1}{2}$ cbm. oxygen, will produce $6192\frac{6}{7} \times \frac{1}{2} = 3096\frac{3}{7}$ calors., forming 1 cbm. CO_2.

The heat produced by 1 kg. pure *fixed carbon*, burnt with $1\frac{1}{3}$ oxygen to CO, and with $2\frac{2}{3}$ kg. O to CO_2, is given differently by various authorities; but the mean of their results is $\frac{5}{7}$ of the heat produced by burning *aeriform* carbon; and this leads to the following simple relation:—

1 kg. of *aeriform carbon*, burnt to CO_2, produces sensible heat .. .. = 11560 calors.
1 kg. of *solid carbon* produces likewise 11560 calors., but in gasifying the fixed carbon $\frac{2}{7} \times 11560$ become latent .. = $3302\frac{6}{7}$ „

And only $\frac{5}{7} \times 11560$ cal... .. .. = $8257\frac{1}{7}$ „
are set free as sensible heat.

1 kg. of *solid carbon*, burnt to CO, produces $\frac{1}{2} \times 11560$ cal. .. .. = 5780 calors.
In gasifying become latent .. .. = $3302\frac{6}{7}$ „

And the sensible heat produced is .. = $2477\frac{1}{7}$ „

Combustion of Hydrocarbons.

If hydrocarbon gases burn with oxygen or air the case is different, because the compound must be decomposed before its components can unite with the oxygen to form the new compounds CO_2 and H_2O.

Decomposing a hydrocarbon gas, or separating the hydrogen contained in it from the carbon, *by the united action of heat and the chemical affinity of oxygen*, will absorb *half* the heat produced by the H in the hydrocarbon; consequently is absorbed or becoming latent:—

Pro 1 cbm. H of atm. density and 0° N (273° absol.)—

$$\frac{3096\frac{3}{7}\text{ cal.}}{2} = 1548\tfrac{3}{14}\text{ calors.}$$

and pro 1 kg. H—

$$\frac{34680\text{ cal.}}{2} = 17340\text{ calors.}$$

We find thus, the products of combustion being cooled down to 0° N (273° N absol.), that—

1 cbm. *methane* of 1 atm. and 273° N absol., burnt with 2 cbm. oxygen, produces $2 \times 6192\frac{6}{7}$ cal. .. .. = $12385\frac{5}{7}$ calors.
Separating 2 cbm. H from C absorbs $2 \times 1548\frac{3}{14}$ cal. .. .. = $3096\frac{3}{7}$ „

Consequently 1 cbm. methane produces *sensible* heat .. .. = $9289\frac{2}{7}$ „
or exactly $\frac{3}{4}$ of what would be due for the 2 cbm. O burnt with it.

1 kg. *methane*, burnt with 4 kg. O, produces 4×4335 cal. .. .. = 17340 calors.
Separating $\frac{1}{4}$ kg. H from C absorbs $\frac{1}{4} \times 17340$ cal. .. .. = 4335 „

Consequently 1 kg. methane produces sensible heat .. .. = 13005 „
Or likewise $\frac{3}{4}$ of what would be due to the 4 kg. O consumed, while $\frac{1}{4}$ of the heat actually produced becomes latent.

In a similar way we find the sensible heat produced by combustion of the total heat due to the O.

1 cbm. ..	burnt with Cbm. O.	Sensible heat. Calors.	1 kg. burnt with Kg. O.	Sensible heat. Calors.	Sensib.	Latent.
Acetylene ..	$2\frac{1}{2}$	$13933\frac{13}{14}$	$3\frac{1}{13}$	$12004\frac{8}{13}$	9/10	1/10
Ethylene ..	3	$15482\frac{1}{7}$	$3\frac{3}{7}$	$12385\frac{5}{7}$	5/6	1/6
Ethane ..	$3\frac{1}{2}$	$17030\frac{5}{14}$	$3\frac{11}{15}$	12716	11/14	3/14
Allylene ..	4	21685	$3\frac{1}{5}$	12138	7/8	1/8
Propylene ..	$4\frac{1}{2}$	$23223\frac{3}{14}$	$3\frac{3}{7}$	$12385\frac{5}{7}$	5/6	1/6
Propane ..	5	$24771\frac{3}{7}$	$3\frac{7}{11}$	$12610\frac{10}{11}$	4/5	1/5
Butylene ..	6	$30964\frac{2}{7}$	$3\frac{3}{7}$	$12385\frac{5}{7}$	5/6	1/6
Butane ..	$6\frac{1}{2}$	$32512\frac{1}{2}$	$3\frac{17}{29}$	$12556\frac{16}{29}$	21/26	5/26
Pentane ..	8	$40253\frac{4}{7}$	$3\frac{5}{9}$	$12523\frac{1}{3}$	25/32	7/32
Benzene gas	$7\frac{1}{2}$	$41801\frac{11}{14}$	$3\frac{1}{13}$	$12004\frac{6}{13}$	9/10	1/10

Combustion of Mixed Gases.

Coal gas, 17 candles. 1 cbm. atm. density, 273° N absolute:—

	Contains litres	Requires oxygen Litres.	Produces sensible heat equal to Litres O.
Methane ..	$370{\cdot}0 \times 2$ =	740·0	$740{\cdot}0 \times \frac{3}{4} = 555{\cdot}00$
Ethylene ..	$25{\cdot}0 \times 3$ =	75·0	$75{\cdot}0 \times \frac{5}{6} = 62{\cdot}50$
Propylene ..	$12{\cdot}0 \times 4\frac{1}{2}$ =	54·0	$54{\cdot}0 \times \frac{5}{6} = 45{\cdot}00$
Benzene ..	$13{\cdot}0 \times 7\frac{1}{2}$ =	97·5	$97{\cdot}5 \times \frac{9}{10} = 87{\cdot}75$
Carbon monoxide	$52{\cdot}5 \times \frac{1}{2}$ =	26·25	26·25
Hydrogen ..	$490{\cdot}0 \times \frac{1}{2}$ =	245·0	245·00
Carbon dioxide	4·0	1237·75	
Nitrogen ..	32·5		
Oxygen	1·0	1·00	1·00

1 cbm. gas = 1000·0 requires 1236·75 O, of which 1032·50 litres O only produce sensible heat, and develope—

$$1036{\cdot}5 \times \frac{867}{140} = 6332{\cdot}196\text{ calors. sensible heat.}$$

One cbm. of this gas weighs 5853/11200 kg.; 1 kg. therefore contains 11200/5853 cbm., will for combustion require 2·36565 cbm. O=3·3795 kg. O, and will produce 12116·965 calors. of sensible heat.

Water Gas, H+CO.—This mixed gas, which consists of equal volumes of H and CO, is formed when steam passes through glowing carbon; the H of the steam is set free, and the O combines with C, forming CO.

One kg. steam of 100° (373° N absol.) consists of 1/9 kg. H and 8/9 kg. O, and forms when passed through glowing carbon, and the product cooled down to 0° N, at atmospheric density; 1/9 kg.=56/45 cbm. H; 8/9 kg. O combines with 6/9 kg. C, forming 14/9 kg.=56·45 cbm. CO; consequently 1 kg. steam and 6/9 kg. C form 15/9 kg.=112/45 cbm. water gas of 0° N (273° N absol.) and atm. density; consequently—

1 kg. water gas = 112/75 cbm., and 1 cbm. = 75/112 kg.
1 kg. water gas contains 3/5 kg. steam + 2/5 kg. C.
1 kg. water gas contains 1/15 kg. H+14/15 CO; =56·75 cbm. H+ 56·75 cbm. CO.
1 cbm. water gas contains ½ cbm. H+½ cbm. CO; =5/112 kg. H+ 5/8 kg. CO.

Production of 1 kg. of water gas of 273° N. absol. requires:—

3/5 kg. of liquid water of 273° N absol. dissolved into H and O by the united action of heat and the chemical affinity of carbon, absorbs, separating 1/15 kg. H from O, 1/15×17340 cal. .. .. =1156 calors.
2/5 kg. solid carbon to gasify absorbs 2/5×3302 6/7 cal. .. .. =1321 1/7 „
2477 1/7 „
2/5 kg. C, burnt with 8/15 kg, O. to form 14/15 kg. CO, produces 8/15×4335 cal.=2312 „

1 kg. water gas requires for its production = 165 1/7 „
1 cbm. of atm. density requires 165 1/7×75/112 kg.= =110 115/196 calors.

Combustion of 1 kg. of Water Gas.

For 1/15 kg. H is required 8/15 kg. O } 16/15 kg. O, which
„ 14/15 „ CO „ 8/15 „ O } produces 4624 calors.

Combustion of 1 cbm. Water Gas.

For 1/2 cbm. H is required 1/4 cbm. O } 1/2 cbm. O, which
„ 1/2 „ CO „ 1/4 „ O } produces 3096 3/7 calors.

(To be continued).

3, Valdemarsgade, Copenhagen, V.
July 27, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Zeitschrift für Anorganische Chemie,
Vol. viii., Parts 1 and 2.

The Atomic and Molecular Solution Volumes.—J. Traube. — This extensive paper has been already noticed.

The Foundations of a New System of the Elements.—J. Traube.—Already inserted.

Critical Studies on the Chemistry of Titanium.—E. A. Schneider.—The results of the above studies may be briefly summarised as—1. The product obtained from potassium titano-fluoride by reduction with sodium in a current of hydrogen contains not only oxygen, but also hydrogen. Whether we have here a titanium hydride, hydroxide, or a case of simple absorption, cannot be decided until chemically pure titanium has been obtained. 2. The assumption that this reduction-product consists exclusively of a lower stage of oxidation of titanium is opposed to the following facts:—*a*. No such lower oxides of titanium have been hitherto isolated. *b*. The melting-point of titanium lies at a very high temperature, as may be learnt from the difficulty of alloying it with copper. 3. There are probably two titanium nitrides. The higher, indigo-blue nitride, passes at a white-heat into the lower and more stable bronze-yellow nitride. 4. The higher nitride can be easily converted into a crystalline titanium sulphide by heating to redness with sulphur in a current of hydrogen. 5. A "titanium chloroform" has not yet proved obtainable. In this respect titanium behaves like tin. On the action of dry hydrochloric acid upon elementary titanium there arises a chlorinised product, not volatile. It must be kept in mind that this reaction may depend upon the presence of a titanium hydroxide or a solid titanium hydride in the elementary titanium.

The Influence of Hydration upon Solubility.—N. Kurnakow.—This paper requires the two accompanying diagrams.

The Solutions of Green Chromium Chloride, $CrCl_3.6H_2O$. — A. Piccini. — The inferences following from the author's results are:—Silver fluoride has, in reference to the green chromium chloride, the property of precipitating that portion of chlorine—or causing it to assume the function of an ion—which is not precipitable by the other silver salts, and in their presence does not act as an ion. In solutions in which the method of the boiling-point indicates little or no dissociation of the green chromium chloride, all the chlorine is precipitated by silver nitrate, whilst in solutions in which dissociation ensues the precipitation is only partial. The solutions of green chromium chloride in methylic alcohol take, in presence of silver nitrate, an intermediate position between the watery solutions and those on ethylic alcohol.

On some New Methods of obtaining Platinous Chlorides, and on the Probable Existence of Platinum Subchloride.—M. Carey Lea.

The Cæsium Double Chlorides, Bromides, and Iodides, with Cobalt and Nickel.—G. F. Campbell.

It is understood that these two papers have appeared also in the English languages.

THE CHEMICAL NEWS.

Vol. LXXII., No. 1869.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Ipswich, 1895.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir Douglas Galton, K.C.B., D.C.L., F.R.S.

(Concluded from p. 136).

Influence of Intercommunication afforded by British Association on Science Progress.

The advances in engineering have produced the steam-engine, the railway, the telegraph, as well as our engines of war, may be said to be the result of commercial enterprise rendered possible only by the advances which have taken place in the several branches of science since 1831. Having regard to the intimate relations which the several sciences bear to each other, it is abundantly clear that much of this progress could not have taken place in the past, nor could further progress take place in the future, without intercommunication between the students of different branches of science.

The founders of the British Association based its claims to utility upon the power it afforded for this intercommunication. Mr. Vernon Harcourt (the uncle of your present General Secretary), in the address he delivered in 1832, said:—"How feeble is man for any purpose when he stands alone—how strong when united with other men!" . . .

I claim for the British Association that it has fulfilled the objects of its founders, that it has had a large share in promoting intercommunication and combination.

Our meetings have been successful because they have maintained the true principles of scientific investigation. We have been able to secure the continued presence and concurrence of the master-spirits of science. They have been willing to sacrifice their leisure, and to promote the welfare of the Association, because the meetings have afforded them the means of advancing the sciences to which they are attached.

The Association has, moreover, justified the views of its founders in promoting intercourse between the pursuers of science, both at home and abroad, in a manner which is afforded by no other agency.

The weekly and sessional reunions of the Royal Society, and the annual *soirées* of other scientific societies, promote this intercourse to some extent; but the British Association presents to the young student, during its week of meetings, easy and continuous social opportunities for making the acquaintance of leaders in science, and thereby obtaining their directing influence.

It thus encourages, in the first place, opportunities of combination, but, what is equally important, it gives at the same time material assistance to the investigators whom it thus brings together.

The reports on the state of science at the present time, as they appear in the last volume of our *Proceedings*, occupy the same important position, as records of science progress, as that occupied by those Reports in our earlier years. We exhibit no symptom of decay.

Science in Germany fostered by the State and Municipalities.

Our neighbours and rivals rely largely upon the guidance of the State for the promotion of both science teaching and of research. In Germany the foundations of technical and industrial training are laid in the Realschulen, and supplemented by the Higher Technical Schools. In Berlin that splendid institution, the Royal Technical High School, casts into the shade the facilities for education in the various Polytechnics which we are now establishing in London. Moreover, it assists the practical workman by a branch department, which is available to the public for testing building materials, metals, paper, oil, and other matters. The standards of all weights and measures used in trade can be purchased from or tested by the Government Department for Weights and Measures.

For developing pure scientific research and for promoting new applications of science to industrial purposes the German Government at the instance of von Helmholtz, and aided by the munificence of Werner von Siemens, created the Physikalische Technische Reichanstalt at Charlottenburg.

This establishment consists of two divisions. The first is charged with pure research, and is at the present time engaged in various thermal, optical, and electrical, and other physical investigations. The second branch is employed in operations of delicate standardising to assist the wants of research students—for instance, dilatation, electrical resistances, electric and other forms of light, pressure gauges, recording instruments, thermometers, pyrometers, tuning-forks, glass, oil-testing apparatus, viscosity of glycerin, &c.

Dr. Kohlrausch succeeded Helmholtz as president, and takes charge of the first division. Professor Hagen, the director under him, has charge of the second division. A professor is in charge of each of the several sub-departments. Under these are various subordinate posts, held by younger men, selected for previous valuable work, and usually for a limited time.

The general supervision is under a Council, consisting of a president, who is a Privy Councillor, and twenty-four members, including the president and director of the Reichsanstalt; of the other members about ten are professors or heads of physical and astronomical observatories connected with the principal universities in Germany. Three are selected from leading firms in Germany representing mechanical, optical, and electric science, and the remainder are principal scientific officials connected with the Departments of War and Marine, the Royal Observatory at Potsdam, and the Royal Commission for Weights and Measures.

This Council meets in the winter, for such time as may be necessary, for examining the research work done in the first division during the previous year, and for laying down the scheme for research for the ensuing year; as well as for suggesting any requisite improvements in the second division. As a consequence of the position which science occupies in connection with the State in Continental countries, the services of those who have distinguished themselves either in the advancement or in the application of science are recognised by the award of honours; and thus the feeling for science is encouraged throughout the nation.

Assistance to Scientific Research in Great Britain.

Great Britain maintained for a long time a leading position among the nations of the world by virtue of the excellence and accuracy of its workmanship, the result of individual energy; but the progress of mechanical science has made accuracy of workmanship the common property of all nations of the world. Our records show that hitherto, in its efforts to maintain its position by the application of science and the prosecution of research, England has made marvellous advances by means of voluntary effort, illustrated by the splendid munificence of such men as Gassiot, Joseph Whitworth, James Mason, and Ludwig Mond; and, whilst the increasing field of scientific research compels us occasionally to seek for

Government assistance, it would be unfortunate if by any change voluntary effort were fettered by State control.

The following are the principal voluntary agencies which help forward scientific research in this country:—The Donation Fund of the Royal Society, derived from its surplus income. The British Association has contributed £60,000 to aid research since its formation. The Royal Institution, founded in the last century, by Count Rumford, for the promotion of research, has assisted the investigations of Davy, of Young, of Faraday, of Frankland, of Tyndall, of Dewar, and of Rayleigh. The City Companies assist scientific research and foster scientific education both by direct contributions and through the City and Guilds Institute. The Commissioners of the Exhibition of 1851 devote £6000 annually to science research scholarships, to enable students who have passed through a college curriculum and have given evidence of capacity for original research to continue the prosecution of science, with a view to its advance or to its application to the industries of the country. Several scientific societies have promoted direct research, each in their own branch of science, out of ther surplus income; and every scientific society largely assists research by the publication, not only of its own proceedings, but often of the work going on abroad in the branch of science which it represents.

The growing abundance of matter year by year increases the burden thus thrown on their finances, and the Treasury has recently granted to the Royal Society £1000 a year, to be spent in aid of the publication of scientific papers not necessarily limited to those of that Society.

The Royal Society has long felt the importance to scientific research of a catalogue of all papers and publications relating to pure and applied science, arranged systematically both as to authors' names and as to subject treated, and the Society has been engaged for some time upon a catalogue of that nature. But the daily increasing magnitude of these publications, coupled with the necessity of issuing the catalogue with adequate promptitude and at appropriate intervals, renders it a task which could only be performed under International co-operation. The officers of the Royal Society have therefore appealed to the Government to urge Foreign Governments to send delegates to a Conference to be held next July to discuss the desirabiilty and the scope of such a catalogue, and the possibility of preparing it.

The universities and colleges distributed over the country, besides their function of teaching, are large promoters of research, and their voluntary exertions are aided in some cases by contributions from Parliament in alleviation of their expenses.

Certain executive departments of the Government carry on research for their own purposes, which in that respect may be classed as voluntary. The Admiralty maintains the Greenwich Observatory, the Hydrographical Department, and various experimental services; and the War Office maintains its numerous scientific departments. The Treasury maintains a valuable chemical laboratory for Inland Revenue, Customs, and agricultural purposes. The Science and Art Department maintains the Royal College of Science, for the education of teachers and students from elementary schools; it allows the scientific apparatus in the National Museum to be used for research purposes by the professors. The Solar Physics Committee, which has carried on numerous researches in solar physics, was appointed by and is responsible to this Department. The Department also administers the Sir Joseph Whitworth engineering research scholarships. Other scientific departments of the Government are aids to research, as, for instance, the Ordnance and the Geological Surveys, the Royal Mint, the Natural History Museum, Kew Gardens, and other lesser establishments in Scotland and Ireland; to which may be added, to some extent, the Standards Department of the Board of Trade, as well as municipal museums, which are gradually spreading over the country.

For direct assistance to voluntary effort the Treasury contributes £4000 a year to the Royal Society for the promotion of research, which is administered under a board whose members represent all branches of Science. The Treasury, moreover, contributes to marine biological observatories, and in recent years has defrayed the cost of various expeditions for biological and astronomical research, which in the case of the *Challenger* expedition involved very large sums of money.

In addition to these direct aids to science, Parliament, under the Local Taxation Act, handed over to the County Councils a sum, which amounted in the year 1893 to £615,000, to be expended on technical education. In many country districts, so far as the advancement of real scientific technical progress in the nation is concerned, much of this money has been wasted for want of knowledge. And whilst it cannot be said that the Government or Parliament have been indifferent to the promotion of scientific education and research, it is a source of regret that the Government did not devote some small portion of this magnificent gift to affording an object-lesson to County Councils in the application of science to technical instruction, which would have suggested the principles which would most usefully guide them in the expenditure of this public money.

Government assistance to science has been based mainly on the principle of helping voluntary effort. The Kew Observatory was initiated as a scientific observatory by the British Association. It is now supported by the Gassiot trust fund, and managed by the Kew Observatory Committee of the Royal Society. Observations on magnetism, on meteorology, and the record of sun-spots, as well as experiments upon new instruments for assisting meteorological, thermometrical, and photographic purposes, are being carried on there. The Committee has also arranged for the verification of scientific measuring instruments, the rating of chronometers, the testing of lenses and of other scientific apparatus. This institution carries on to a limited extent some small portion of the class of work done in Germany by that magnificent institution, the Reichsanstalt at Charlottenburg, but its development is fettered by want of funds. British students of science are compelled to resort to Berlin and Paris when they require to compare their more delicate instruments and apparatus with recognised standards. There could scarcely be a more advantageous addition to the assistance which Government now gives to science than for it to allot a substantial annual sum to the extension of the Kew Observatory, in order to develop it on the model of the Reichsanstalt. It might advantageously retain its connection with the Royal Society, under a Committee of Management representative of the various branches of science concerned, and of all parts of Great Britain.

CONCLUSION.

The various agencies for scientific education have produced numerous students admirably qualified to pursue research; and at the same time almost every field of industry presents openings for improvement through the development of scientific methods. For instance, agricultural operations alone offer openings for research to the biologist, the chemist, the physicist, the geologist, the engineer, which have hitherto been largely overlooked. If students do not easily find employment, it is chiefly attributable to a want of appreciation for science in the nation at large.

This want of appreciation appears to arise from the fact that those who nearly half a century ago directed the movement of national education were trained in early life in the universities, in which the value of scientific methods was not at that time fully recognised. Hence our elementary, and even our secondary and great public schools, neglected for a long time to encourage the spirit of investigation which develops originality. This defect is diminishing daily.

There is, however, a more intangible cause which may have had influence on the want of appreciation of science by the nation. The Government, which largely profits by science, aids it with money, but it has done very little to develop the national appreciation for science by recognising that its leaders are worthy of honours conferred by the State. Science is not fashionable, and science students—upon whose efforts our progress as a nation so largely depends—have not received the same measure of recognition which the State awards to services rendered by its own officials, by politicians, and by the Army and by the Navy, whose success in future wars will largely depend on the effective applications of science.

The Reports of the British Association afford a complete chronicle of the gradual growth of scientific knowledge since 1831. They show that the Association has fulfilled the objects of its founders in promoting and disseminating a knowledge of science throughout the nation.

The growing connection between the sciences places our annual meeting in the position of an arena where representatives of the different sciences have the opportunity of criticising new discoveries and testing the value of fresh proposals, and the Presidential and Sectional Addresses operate as an annual stock-taking of progress in the several branches of science represented in the Sections. Every year the field of usefulness of the Association is widening. For, whether with the geologist we seek to write the history of the crust of the earth, or with the biologist to trace out the evolution of its inhabitants, or whether with the astronomer, the chemist, and the physicist we endeavour to unravel the constitution of the sun and the planets or the genesis of the nebulæ and stars which make up the universe, on every side we find ourselves surrounded by mysteries which await solution. We are only at the beginning of work.

I have, therefore, full confidence that the future records of the British Association will chronicle a still greater progress than that already achieved, and that the British nation will maintain its leading position amongst the nations of the world, if it will energetically continue its voluntary efforts to promote research, supplemented by that additional help from the Government, which ought never to be withheld when a clear case of scientific utility has been established.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

IPSWICH, 1895.

By Prof. RAPHAEL MELDOLA, F.R.S., F.I.C., For. Sec. C.S., President of the Section.

THE STATE OF CHEMICAL SCIENCE IN 1851.

In order to estimate the progress of chemical science since the year 1851, when the British Association last met in this town, it will be of interest for us to endeavour to place ourselves in the position of those who took part in the proceedings of Section B on that occasion. Perhaps the best way of performing this retrograde feat will be to confront the fundamental doctrines of modern chemistry with the state of chemical theory at that period, because at any point in the history of a science the theoretical conceptions in vogue—whether these conceptions have survived to the present time or not—may be taken as the abstract summation of the facts, *i.e.*, of the real and tangible knowledge existing at the period chosen as the standard of reference.

Without going too far back in time I may remind you that in 1811 the atomic theory of the chemists was grafted on to the kindred science of physics through the enunciation of the law associated with the name of Avogadro di Quaregna. The rationalising of this law had been accomplished in 1845; but the kinetic theory of gases, which had been foreshadowed by D. Bernoulli in 1738, and in later times by Herapath, Joule, and Krönig, lay buried in the archives of the Royal Society until recently unearthed by Lord Rayleigh and given to the world in 1892 under the authorship of Waterston, the legitimate discoverer. The later developments of this theory did not take place till after the last Ipswich meeting, viz., in 1857—1862, by Clausius, and by Clerk Maxwell in 1860—1867. Thus the kinetic theory of gases of the physicists had not in 1851 acquired the full significance for chemists which it now possesses; the hypothesis of Avogadro was available, analogous conceptions had been advanced by Davy in 1812, and by Ampère in 1814; but no substantial chemical reasons for its adoption were adduced until the year 1846, when Laurent published his work on the law of even numbers of atoms and the nature of the elements in the free state (*Ann. Chim. Phys.* [3], xviii., 266).

The so-called "New Chemistry," with which students of the present time are familiar, was, in fact, being evolved about the period when the British Association last assembled at Ipswich; but it was not till some years later, and then chiefly through the writings of Laurent and Gerhardt, that the modern views became accepted. It is of interest to note in passing that the nomenclature of organic compounds formed the subject of a report by Dr. Daubeny at that meeting, in which he says:—"It has struck me as a matter of surprise that none of the British treatises on Chemistry with which I am acquainted should contain any rules to guide us, either in affixing names to substances newly discovered or in divining the nature and relations of bodies from the appellations attached to them. Nor do I find this deficiency supplied in a manner which to me appears satisfactory when I turn to the writings of Continental chemists." In a subsequent portion of the report Dr. Daubeny adds:—"No name ought, for the sake of convenience, to exceed in length six or seven syllables." I am afraid the requirements of modern organic chemistry have not enabled us to comply with this condition.

Among other physical discoveries which have exerted an important influence on chemical theory, the law of Dulong and Petit, indicating the relationship between specific heat and atomic weight, had been announced in 1819, had been subsequently extended to compounds by Neumann, and still later had been placed upon a sure basis by the classical researches of Regnault in 1839. But here, again, it was not till after 1851 that Cannizzaro (1858) gave this law the importance which it now possesses in connection with the determination of atomic weights. Thermo-chemistry as a distinct branch of our science may also be considered to have arisen since 1851, although the foundations were laid before this period by the work of Favre and Silbermann, Andrews, Graham, and especially Hess, whose important generalisation was announced in 1840, and whose claim to just recognition in the history of physical chemistry has been ably advocated in recent times by Ostwald. But the elaboration of thermochemical facts and views in the light of the dynamical theory of heat was first commenced in 1853 by Julius Thomsen, and has since been carried on concurrently with the work of Berthelot in the same field which the latter investigator entered in 1865. Electro-chemistry in 1851 was in an equally rudimentary condition. Davy had published his electro-chemical theory in 1807, and in 1812 Berzelius had put forward those views on electric affinity which became the basis of his dualistic system of formulation. In 1833 Faraday announced his famous law of electro-chemical equivalence, which gave a fatal blow to the conception of Berzelius, and which later (1839—1840) was made use of by Daniell in order to show the untenability of the dualistic system. By 1851 the views of Berzelius had been abandoned, and, so far as chemical theory is concerned, the whole subject may be considered to have been in abeyance at that time. It is of interest to note, however, that in that year Williamson advanced, on quite distinct grounds, his now well-known theory of atomic interchange between molecules, which theory in a more extended form was developed independently from the physical side and applied to electrolytes by Clausius in 1857. The modern theory of electrolysis associated with the names of Arrhenius, van 't Hoff, and Ostwald, is of comparatively recent growth. It appears that Hittorf, in 1878, was the first to point out the relationship between electrolytic conductivity and chemical activity, this same author as far back as 1856 having combated the prevailing view that the electric current during electrolysis does the work of overcoming the affinities of the ions. Arrhenius formulated his theory of electrolytic dissociation in 1887, Planck having almost simultaneously arrived at similar views on other grounds.

Closely connected with electrolysis is the question of the constitution of solutions, and here again a convergence of work from several distinct fields has led to the creation of a new branch of physical chemistry which may be considered a modern growth. The relationship between the strength of a solution and its freezing-point had been discovered by Blagden towards the end of the last century, but in 1851 chemists had no notion that this observation would have any influence on the future development of their science. Another decade elapsed before the law was re-discovered by Rudorff (1861), and ten years later was further elaborated by de Coppet. Raoult published his first work on the freezing-point of solutions in 1882, and two years later the relationship between osmotic pressure and the lowering of freezing-point was established by H. de Vries, who first approached the subject as a physiologist, through observations on the cell-contents of living plants. As the work done in connection with osmotic pressure has had such an important influence on the "dissociation" theory of solutions, it will be of interest to note that at the last Ipswich meeting Thomas Graham made a communication on liquid diffusion, in which he "gave a view of some of the unpublished results, to ascertain whether solutions of saline bodies had a power of diffusion among liquids, especially water." In 1877 Pfeffer, who, like de Vries, entered the field from the botanical physiological side, succeeded in effecting the measurement of osmotic pressure. Ten years later van 't Hoff formulated the modern dissociation theory of solution by applying to dissolved substances the laws of Boyle, Gay-Lussac, and Avogadro, the law of osmotic pressure, and Raoult's law connecting the depression of freezing-point with molecular weight, thus laying the foundation of a doctrine which, whether destined to survive in its present form or not, has certainly exerted a great influence on contemporary chemical thought.

Consider, further, the state of knowledge in 1851 concerning such leading principles as dissociation or thermolysis, mass action and chemical equilibrium. Abnormal vapour densities had been observed by Avogadro in 1811, and by Ampère in 1814. Grove had dissociated water vapour by heat in 1847, but the first great advance was made ten years later by Sainte-Claire Deville, from whose work has emanated our existing knowledge of this subject. I may add that the application of this principle to explain the cases of abnormal vapour density was made in 1858 by Kopp, Kekulé, and Cannizzaro, almost simultaneously; but, strangely enough, this explanation was accepted by Deville himself. The subsequent stages are subjects of modern history. The current views on mass action were foreshadowed, as is well known, by Berthollet in his "Statique Chimique," published in 1803, but no great advance had been made when the British Association last met here. The subject first began to assume a quantitative aspect through the researches of Bunsen and Debus in 1853, and was much advanced by Gladstone in 1865, and by Harcourt and Esson a year later. Goldberg and Waage published their classical work on this subject in 1867.

Equally striking will appear the advances made since 1851 if we consider that the whole subject of spectrum analysis, which brings our science into relationship with astronomy, has been called into existence since that date. The celebrated work of Bunsen and Kirchhoff was not published till 1859. Neither can I refrain from reminding you that the coal-tar colour industry, with which I have been to a small extent connected, was started into activity by Perkin's discovery of mauve in 1856; the reaction of this industry on the development of organic chemistry is now too well known to require further mention. In that direction also which brings chemistry into relationship with biology, the progress has been so great that it is not going beyond the fact to stat that a new science has been created. Pasteur began his studies on fermentation in 1857, and out of that work has arisen the science of bacteriology, with its multifarious and far-reaching consequences. As this chapter of chemical history forms the subject of one of the evening discourses at the present meeting, it is unnecessary to dwell further upon it now. One other generalisation may be chronicled among the great developments achieved since 1851. I refer to the periodic law connecting the atomic weights of the chemical elements with their physical and chemical properties. Attempts to establish numerical relationships in the case of isolated groups of elements had been made by Döbereiner in 1817, by Gmelin in 1826, and again by Döbereiner in 1829. The triad system of grouping was furtser developed by Dumas in 1851. I am informed by Dr. Gladstone that at the last Ipswich meeting Dumas' speculations in this direction excited much interest. All the later steps of importance have, however, been made since that time, viz., by de Chancourtois in 1862, the "law of octaves" by Newlands in 1864, the periodic law by Mendeleeff, and almost contemporaneously by Lothar Meyer, in 1869.

I have been tempted into giving this necessarily fragmentary and possibly tedious historical sketch because it is approaching half a century since the British Association visited this town, and the opportunity seemed favourable for going through that process which in commercial affairs is called "taking stock." The result speaks for itself. Our students of the present time who are nourished intellectually by these doctrines should be made to realise how rapid has been their development. The pioneers of our science on whose shoulders we stand —and many of whom are happily still among us—will derive satisfaction from the retrospect, and will admit that their labours have borne goodly fruit. It is not, however, simply for the purpose of recording this enormons progress that I have ventured to assume the office of stock-taker. The year 1851 may be regarded as occurring towards the close of one epoch and the dawn of a new era in chemical history. Consider broadly the state of organic chemistry at that time. There is no occasion for going into detail, even if time admitted, because our literature has recently been enriched by the concise and excellent historical works of Schorlemmer, and of Ernst von Meyer. It will suffice to mention that the work and writings of Liebig, Berzelius, Wöhler, Dumas, Gay-Lussac, Bunsen, and others, had given us the leading ideas of isomerism, substitution, compound radicles, and types. Wurtz and Hofmann had just discovered the organic ammonias; Williamson that same year made known his celebrated work on the ethers; and Gerhardt discovered the acid anhydrides a year later. The newer theory of types was undergoing development by Gerhardt and his followers; the mature results were published in the fourth volume of the "Traité de Chimie" in 1856. In this country the theory was much advanced by the writings of Odling and Williamson.

SUBSEQUENT DEVELOPMENT OF CHEMISTRY ALONG TWO LINES.

The new era which was dawning upon us in 1851 was that of structural or constitutional chemistry, based on the doctrine of the valency of the atoms. It is well known that this conception was broached by Frankland in 1852, as the result of his investigations on the organo-metallic compounds. But it was not till 1858 that Kekulé, who had previously done much to develop the theory of types, and Couper, almost simultaneously, recognised the quadrivalent character of carbon. To attempt to give anything approaching an adequate notion of the subsequent influence of this idea on the progress of organic chemistry would be tantamount to reviewing the present condition of that subject. I imagine that no conception more prolific of results has ever been introduced into any department of science. If we glance back along the stream it will be seen that shortly after the last meeting here the course of discovery began to concentrate itself into two channels. In one we now find the results of the confluent labours of those who have regarded our science from its physical side. In the other channel is flowing the tide of discovery arising from the valency doctrine and its extension to the structure of chemical molecules. The two channels are at present fairly parallel and not far apart; an occasional explorer endeavours now and again to make a cross-cut so as to put the streams into communication. The currents in both are running very rapidly, and the worker who has embarked on one or the other finds himself hurried along at such a pace that there is hardly breathing time to step ashore and see what his neighbours are doing. It speaks well for the fertility of the conception of valency that the current in this channel is flowing with unabated vigour, although its catchment area—to pursue the metaphor—is by no means so extensive as that of the neighbouring stream.

The modern tendency to specialisation, which is a necessity arising from the large number of workers and the rapid multiplication of results, is apparently in the two directions indicated. We have one class of workers dealing with the physics of matter in relation to general chemical properties, and another class of investigators concerning themselves with the special properties of individual compounds and classes of compounds—with atomic idiosyncracies. The workers of one class are differentiating while their colleagues are integrating. It would be nothing less than unscientific to institute a comparison between the relative merits of the two methods; both are necessary for the development of our science. All methods of attacking the unknown are equally welcomed. In some cases physical methods are available; in other cases purely chemical methods have alone been found of use. There is no antagonism, but co-operation. If the results of the two methods are sometimes at variance it is simply because we have not known how to interpret them. The physical chemist has adopted the results of the application of chemical methods of determining "constitution," and is endeavouring to furnish us with new weapons for attacking this same problem. The chemist who is seeking to unravel the architecture of molecules is dependent at the outset upon physical methods of determining the relative weights of his molecules. The worker who is bringing about new atomic groupings is furnishing material for the further development of generalisations from which new methods applicable to the problem of chemical structure may again be evolved. The physical chemist sometimes, from the broadness of his view, is apt to overlook or to minimise the importance of chemical individuality. On the other hand, the chemist who is studying the numberless potentialities of combination resident in the atoms, and who has grasped to the full extent their marvellous individualities, is equally liable to forget that there are connecting relationships as well as specific differences in the properties of elements and compounds. These are but the mental traits—the unconscious bias engendered by the necessary specialisation of work to which I have referred, and which is observable in every department of scientific labour.

The Present State of Structural Chemistry.

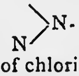
The success attending the application of the doctrine of valency to the compounds of carbon has helped its extension to all compounds formed by other elements, and the student of the present day is taught to use structural formulæ as the A B C of his science. It is, I think, generally recognised among chemists that this doctrine in its present state is empirical, but it does not appear to me that this point is sufficiently insisted upon in chemical teaching. I do not mean to assert that for the last thirty years chemists have been pursuing a phantom; neither do I think that we should be justified in applying to this doctrine the words applied to its forerunner, the "types" of Gerhardt, by Lothar Meyer, who says that these "have rendered great service in the development of the science, but they can only be regarded as a part of the scaffolding which was removed when the erection of the system of organic chemistry had made sufficient progress to be able to dispense with it" ("Modern Theories of Chemistry," p. 194). It appears to me, on the contrary, that there is a physical reality underlying the conception of valency, if for no other reason because of the conformability of this property of the atoms to the periodic law. But the doctrine as it stands is empirical, in so far that it is only representative and not explanatory. Frankland and Kekulé have given us a great truth, but its very success is now making it more and more obvious that it is a truth which is pressing for further development from the physical side. If we are asked why CO exists, and why CH_2 and CCl_2 do not, together with innumerable similar questions which the inquisitive mind will raise, we get no light from this doctrine. If any over-sanguine disciple goes so far as to assert that all the possible compounds of the elements indicated by their valency are capable of existence, and will sooner or later be prepared, he will, I imagine, find himself rapidly travelling away from the region of fact.

There is something to be reckoned with besides valency. The one great desideratum of modern chemistry is unquestionably a physical or mechanical interpretation of the combining capacities of the atoms. Attempts at the construction of such theories have been made, but thus far only in a tentative way, and these views cannot be said to have yet come within the domain of practical chemical politics. I have in mind, among other suggestions, the dynamical theory of van 't Hoff, published in 1881 ("Ansichten über die organische Chemie"), the theory of electric charges on the atoms broached by Johnstone Stoney in 1874, and so ably advocated by the late Professor v. Helmholtz in his Faraday lecture in 1881, and the electric polar theory of Victor Meyer and Riecke, published in 1888 ("Einige Bemerkungen über den Kohlenstoffatom und die Valenz," *Ber.*, xxi., 946, 1620).

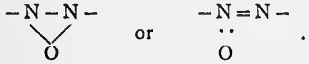
Pending the rationalisation of the doctrine of valency, its promulgation must continue in its present form. Its services in the construction of rational formulæ, especially within the limits of isomerism, have been incalculable. It is the ladder by which we have climbed to the present brilliant achievements in chemical synthesis, and we are not in a position to perform the ungracious task of kicking it away. In recalling attention to its weaknesses I am only putting myself in the position of the physician who diagnoses his patient's case with the ulterior object of getting him strengthened. There can be no doubt that renewed vitality has been given to the doctrine by the conceptions of tautomerism and desmotropy, formulated by Conrad Laar in 1885, and by Paul Jacobson in 1887. The importance of these ideas is becoming more evident with the advancement of chemical discovery. Any attempt to break down the rigidly statical conception of our structural formulæ appears to me to be a step in the right direction. Then, again, I will remind you of the prolific development of the doctrine in the hands of Le Bel and van 't Hoff by the introduction of the stereochemical hypothesis in 1874—unquestionably the greatest advance in structural chemistry since the recognition of the quadrivalent character of the carbon atom. If evidence be required that there is a physical reality underlying the conception of valency, we need only point to the close accordance of this notion of the asymmetric carbon atom with the facts of so-called "physical isomerism" and the splendid results that have followed from its introduction into our science, especially in the field of the carbohydrates, through the investigations of Emil Fischer and his pupils. In other directions the stereochemical hypothesis has proved to be a most suggestive guide. It was applied by Professor v. Baeyer in 1885 (*Ber.*, xviii., 2277) to explain the conditions of stability or instability of certain atomic groupings, such as the explosiveness of polyacetylene compounds and the stability of penta- and hexa-cyclic systems. Again, in 1888 this eminent chemist showed its fertility in a series of brilliant researches upon benzene derivatives (*Ann.*, cxxxvii., 158, and subsequent papers). Nor can I omit to mention the great impetus given in this field by the classical work of Wislicenus, who in 1887 applied the hypothesis to unsaturated compounds and to cyclic systems with remarkable success ("Ueber die räumliche Anordnung der Atome in organischen Molekülen," &c.). Quite recently Victor Meyer and J. Sudborough have shown that the ability of certain derivatives of benzoic and naphthoic acids to form ethers is governed by stereochemical considerations (*Ber.*, xxvii., 510, 1580, 3146, and xxviii., 182, 1254). But I must avoid the temptation to enlarge upon this theme, because the whole subject has been recently brought together by C. A. Bischoff in his "Handbuch der Stereochemie" (Frankfurt, 1893-94), a work to which all who are interested in the subject will naturally turn for reference.

While the present advanced state of structural chemistry may thus be looked upon as the outcome of the conceptions of Frankland and Kekulé, it may be well to bear in mind that the idea of structure is not *necessarily* bound up with the hypothesis of valency in its present form. Indeed, some advance had been made in representing "constitution," especially by Kolbe, before the formal introduction of this hypothesis. The two ideas have grown up together, but the experimental evidence that in any molecule the atoms are grouped together in a particular way is really independent of any theory of valency. It is only after this evidence has been acquired, either by analysis or synthesis, that we proceed to apply the hypothesis in building up the structural formula. It is of course legitimate to assume the truth of the hypothesis, and to endeavour by its use to convert an empirical into a rational formula; but this method generally gives us a choice of formulæ from which the true one can only be selected by further experimental investigation. Even within the narrower limits of isomerism it is by no means certain that all the modifications of a compound indicated by hypothesis are actually capable of existence. There is, for example, evidence that some of the "position isomerides" among the derivatives of mono- and polycyclic compounds are too unstable to exist—a fact which in itself is sufficient to indicate the necessity for a revision and extension of our notions of valency. Thus, by way of illustration, there is nothing in the hypothesis to indicate why orthoquinones of the benzene series should not be capable of existence; yet it is a fact that in spite of all efforts such compounds have never been obtained. The conditions essential for the existence of these compounds appear to be that the hydrogen of the benzene ring should be replaced by acid substituents such as oxygen, hydroxyl, chlorine, or bromine. Under these circumstances, as Zincke has shown (*Ber.*, xx., 1776), tetrachlor and tetrabrom-orthobenzoquinone are stable compounds. So also the interesting researches of Nietzki have proved that in such a compound as rhodizonic acid (*Ber.*, xix., 308, and xxiii., 3136) orthoquinone oxygen atoms are present. But there is nothing in the doctrine of valency which leads us to suspect that these orthoquinone derivatives can exist while their parent compound resists all attempts at isolation. I am aware that it is dangerous to argue from negative evidence, and it would be rash to assert that these orthoquinones will never be obtained. But even in the present state of knowledge it may be distinctly affirmed that the methods which readily furnish an orthoquinone of naphthalene completely fail in the case of benzene, and it is just on such points as this that the inadequacy of the hypothesis becomes apparent. In other words, the doctrine fails in the fundamental requirement of a scientific theory; in its present form it gives us no power of prevision—it hints at possibilities of atomic groupings, but it does not tell us *à priori* which of these groupings are likely to be stable and which unstable. I am not without hope that the next great advance in the required direction may yet come from the stereochemical extension of the hypothesis, although the attempts which have hitherto been made to supply its deficiencies cannot but be regarded as more or less tentative.

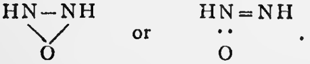
THE NEW THEORY OF ABSTRACT TYPES.

I will venture, in the next place, to direct attention to a modern development of structural chemistry which will help to illustrate still further some of the points raised. For many years we have been in the habit of abstracting from our structural formulæ certain ideal complexes of atoms which we consider to represent the nucleus or type from which the compound of known constitution is derived. In other words the hypothesis of valency which was developed originally from Gerhardt's types is now leading us back to another theory of types based upon a more intimate knowledge of atomic grouping within the molecule. In some cases these types have been shown to be capable of existence; in others they are still ideal. Used in this way the doctrine of valency is most suggestive, but at the same time its lack of prevision is constantly forcing itself upon the attention of chemical investigators. The parent compound has sometimes been known before its derivatives, as in the case of ammonia, which was known long before the organic amines and amides. In other instances the derivatives were obtained before the type was isolated, as in the case of the hydrazines, which were characterised by Emil Fischer in 1875, and the hydrazo-compounds, which have been known since 1863, while hydrazine itself was first obtained by Curtius in 1887. Phenylazimide was discovered by Griess in 1864, and many representatives of this group have been since prepared; but the parent compound, hydrazoic acid, was only isolated by Curtius in 1890. Derivatives of triazole and tetrazole were obtained by Bladin in 1885; the types were isolated by this chemist and by Andreocci in 1892. Pyrazole derivatives were prepared by Knorr in 1883; pyrazole itself was not isolated till 1889, by Buchner. Alkyl nitramides were discovered by Franchimont and Klobbie many years before the typical compound, nitramide, $NO_2.NH_2$, which was isolated last year by Thiele and Lachman (*Ber.*, xxvii., 1909). Examples might be multiplied to a formidable extent, but enough have been given to illustrate the principle of the erection of types, which were at first imaginary, but which have since become real. The utility of the hypothesis is undeniable in these cases, and we are justified in pushing it to its extreme limits. But no chemist, even if endowed with prophetic instinct, could have certainly foretold six years ago that the type of Griess's "triazobenzene would be capable of free existence, and still less that when obtained it would prove to be a strong acid. The fact, established by Curtius, that the group  $\genfrac{}{}{0pt}{}{\diagdown}{N\diagup}\!\!>\!N-$ functions in chemical molecules like the atom of chlorine is certainly among the most striking of recent discoveries. Only last year the list of nitrogen compounds was enriched by the addition of $CO(N_3)_2$, the nitrogen analogue of phosgene (Curtius, *Ber.*, xxvii., 2684).

These illustrations, drawn from the compounds of nitrogen, will serve to bring out the wonderful development which our knowledge of the chemistry of this element has undergone within the last few years. I might be tempted here into a digression on the general bearing of the very striking fact that an element comparatively inactive in the free state should be so remarkably active in combination, but I must keep to the main topic, as by means of these compounds it is possible to illustrate still further both the strength and the weakness of our modern conceptions of chemical structure. Consider some of the undiscovered compounds which are foreshadowed by the process of ideal abstraction of types. The azoxy-compounds contain the complex

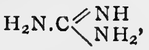


The types would be—



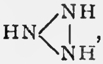
The first of these formulæ represents the unknown dihydronitrous oxide. The azo-compounds are derivatives of the hypothetical diimide HN : NH. An attempt to prepare this compound from azodicarbonic acid (Thiele, *Ann.*, cclxxi., 130) resulted in the formation of hydrazine. The diethyl-derivative may have been obtained by Harries (*Ber.*, xxvii., 2276), but this is doubtful. It is at present inexplicable why compounds in which the group · N : N · is in combination with aromatic radicles should be so remarkably stable, while the parent compound appears to be incapable of existence. The addition of two atoms of hydrogen converts this type again into a stable compound. There is nothing in the structural formulæ to indicate these facts. The amidines are stable compounds, and the so called "anhydro-bases," or imidazoles, are remarkably stable; the parent compound—

has not been obtained, while its amido-derivative—

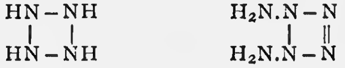


is the well-known substance, guanidine. The isodiazo-compounds recently discovered by Schraube and Schmidt and by Bamberger (*Ber.*, xxvii., 514, 679, &c.) are possibly derivatives of the hypothetical substance O : N.NH$_2$, which might be named nitrosamide. Why this compound should not exist as well as nitramide is another question raised by the principle of abstract types. The carbizines were formerly regarded as derivatives of the compounds—

(Fischer, *Ann.*, ccxii., 326; Freund and Goldsmith, *Ber.*, xxi., 2456). Although this structure has now been disproved the possible existence of the types has been suggested. Carbizine and thiocarbizine differ from urea and thiocarbamide only by two atoms of hydrogen. These types have not been isolated; if they are incapable of existence the current views of molecular structure give no suggestion of a reason. The diazoamides are derivatives of the hypothetical H$_2$N.NH.NH$_2$ or HN : N.NH$_2$, compounds which Curtius speaks of as the propane and propylene of the nitrogen series. The latter complex was at one time thought to exist in diazohippuramide (*Ber.*, xxiv., 3342; this has since been shown to be hippurazide, *i.e.*, a derivative of N$_3$H (*Ber.*, xxvii., 779), and a biacidyl derivative of the former type has also been obtained (*Ber.*, 3344). Both these types await isolation if they are capable of existence. I may add that several attempts to convert diazoamides into dihydro-derivatives by mild alkaline reduction have led me to doubt whether this nitrogen chain can exist in combination with hydrocarbon radicles. The bisdiazoamides of H. v. Pechmann and Frobenius (*Ber.*, xxvii., 898) are derivatives of the 5-atom chain H$_2$N.NH.NH.NH.NH$_2$ or HN : N.NH.N : NH, a type which hardly seems likely to be of sufficient stability to exist. The tetrazones of Emil Fischer have for their type the 4-atom chain H$_2$N.N : N.NH$_2$ or H$_2$N.NH.NH.NH$_2$, of which the free existence is equally problematical, although a derivative containing the chain – N:N.NH.NH – has been obtained by Curtius (*Ber.*, xxvi., 1263). Hydrazoic acid may be regarded as a derivative of triimide—



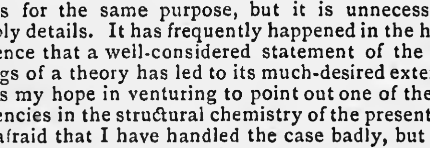
but this type appears to be also incapable of isolation (Curtius, *Ber.*, xxvi., 407). The hydrazidines or formazyls of Pinner (*Ber.*, xvii., 182) and of H. v. Pechmann (*Ber.*, xxv., 3175) have for their parent compound the hypothetical substance H$_2$N.N : CH.N : NH. In 1888 Limpricht described certain azo-compounds (*Ber.*, xxi., 3422) which, if possessing the structure assigned by that author, must be regarded as derivatives of diamidotetrimide—



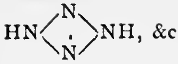
Both these types are at present imaginary; whether it is possible for cyclic nitrogen systems to exist we have no means of knowing—all that can be said is that they have never yet been obtained. It is possible, as I pointed out in 1890 at the Leeds meeting of the British Association, that mixed diazoamides may be derivatives of such a 4-atom ring.

Any chemist who has followed the later developments of the chemistry of nitrogen could supply numerous other instances of undiscovered types. A chapter on the unknown compounds of this element would furnish quite an exciting addition to many of those books which are turned out at the present time in such profusion to meet the requirements of this or that examining body. I have selected my examples from these compounds simply because I can claim some of them as personal acquaintances. It would be easy to make use of carbon compounds for the same purpose, but it is unnecessary to multiply details. It has frequently happened in the history of science that a well-considered statement of the shortcomings of a theory has led to its much-desired extension. This is my hope in venturing to point out one of the chief deficiencies in the structural chemistry of the present time. I am afraid that I have handled the case badly, but I am bound to confess that I am influenced by the same feelings as those which prevent us from judging an old and well-tried friend too severely.

The theory of types to which we have reverted as the outcome of the study of molecular structure is capable of almost indefinite extension if, as there is good reason for doing, we replace atoms or groups by their valency analogues in the way of other atoms or groups of atoms. The facts that in cyclic systems N can replace CH (benzene and pyridine), that O, S, and NH are analogues in furfurane, thiophene, and pyrrole, are among the most familiar examples. The remarkable iodo- and iodoso-compounds recently discovered by Victor Meyer and his colleagues are the first known instances in which the trivalent atom of iodine has been shown to be the valency analogue of nitrogen in organic combination. Pushing this principle to the extreme we get further suggestions for new groupings, but, as before, no certainty of prevision. Thus, if nitrogen formed the oxide N$_2$O$_2$ the series might be written—

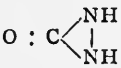


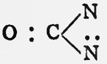
Of course these formulæ are more or less conjectural, being based on valency only. But since nitrous oxide is the analogue of hydrazoic acid, they hint at the possibility of such compounds as—


$HN\left\langle\begin{matrix}N\\ \cdot\\ N\end{matrix}\right\rangle NH$, &c.

If a student produced a set of formulæ corresponding to the above, in which NH had been substituted for O, and asked whether they did not indicate the existence of a whole series of unknown hydrogen compounds of nitrogen, we should probably tell him that his notions of chemical structure had run wild. At the same time I am bound to admit that it would be very difficult, if not impossible, to furnish him with satisfactory reasons for believing that such groupings are improbable. Compare again the series—

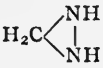

$O : C\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.$ (1)

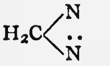

$O : C\left\langle\begin{matrix}NH\\ |\\ NH\end{matrix}\right.$ (2)


$O : C\left\langle\begin{matrix}N\\ \cdot\cdot\\ N\end{matrix}\right.$ (3)


$O : C\left\langle\begin{matrix}NO_2\\NO_2\end{matrix}\right.$ (4)


$H_2C\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.$ (5)


$H_2C\left\langle\begin{matrix}NH\\ |\\ NH\end{matrix}\right.$ (6)


$H_2C\left\langle\begin{matrix}N\\ \cdot\cdot\\ N\end{matrix}\right.$ (7)


$H_2C\left\langle\begin{matrix}NO_2\\NO_2\end{matrix}\right.$ (8)

The first is urea; the second, third, fourth, fifth (methylene diamine), and sixth are unknown; the seventh is the remarkably interesting diazomethane discovered last year by H. v. Pechmann (*Ber.*, xxvii., 1888). The last compound, dinitromethane, is known in the form of its salts, but appears to be incapable of existence in the free state. There is nothing expressed or implied in the existing theory of chemical structure to explain why dinitromethane is unstable while trinitromethane is stable, and mono- and tetranitromethane so stable as to admit of being distilled without decomposition. Chemists will form their own views as to the possibility or impossibility of such a series as this being completed. Whether there would be a concordance of opinion I will not venture to say: but any chemist who expressed either belief or disbelief with regard to any special member would, I imagine, have great difficulty in giving a scientific reason for the faith which is in him. At the most he would have only the very unsafe guide of analogy to fall back upon. Perhaps by the time the British Association holds its next meeting at Ipswich it will have became possible to prove that one particular configuration of certain atoms is possible and another configuration impossible. Then will have been achieved that great advance for which we are waiting—the reunion of the two streams into which our science began to diverge shortly after the last Ipswich meeting.

The present position of structural chemistry may be summed up in the statement that we have gained an enormous insight into the anatomy of molecules, while our knowledge of their physiology is as yet in a rudimentary condition. In the course of the foregoing remarks I have endeavoured to indicate the direction in which our theoretical conceptions are most urgently pressing for extension. It is, perhaps, as yet premature to pronounce an opinion as to whether the next development is to be looked for from the stereochemical side; but it is not going too far to express once again the hope that the geometrical representation of valency will give us a deeper insight into the conditions which determine the stability of atomic configurations. The speculations of A. v. Baeyer, Wislicenus, Victor Meyer, Wunderlich, Bischoff, and others have certainly turned the attention of chemists towards a quarter from which a new light may eventually dawn.

The Progress of Synthetical Chemistry.

If, in my earnest desire to see the foundations of structural chemistry made more secure, I may have unwittingly given rise to the impression that I am depreciating its services as a scientific weapon, let me at once hasten to make amends by directing attention to the greatest of its triumphs, the synthesis of natural products, *i.e.*, of compounds which are known to be produced by the vital processes of animals and plants.

Having been unable to find any recent list of the natural compounds which have been synthesised, I have compiled a set of tables which will, I hope, see the light at no very distant period. According to this census we have now realised about 180 such syntheses. The products of Bacteria have been included in the list because these compounds are the results of vital activity in the same sense that alcohol is a product of the vital activity of the yeast plant. On the other hand, the various uro-compounds resulting from the transformation in the animal economy of definite chemical substances administered for experimental purposes have been excluded, because I am confining my attention to natural products. Of course, the importance of tracing the action of the living organism on compounds of known constitution from the physiological point of view cannot be over-estimated. Such experiments will, without doubt, in time shed much light on the working of the vital laboratory.

The history of chemical synthesis has been so thoroughly dealt with from time to time that I should not have ventured to obtrude any further notice of this subject upon your patience were it not for a certain point which appeared to me of sufficient interest to merit re-consideration. It is generally stated that the formation of urea from ammonium cyanate by Wöhler in 1828 was the first synthesis of an organic compound. There can be no doubt that this discovery, which attracted much attention at the time, gave a serious blow to the current conceptions of organic chemistry, because urea was so obviously a product of the living animal. It will be found, however, that about the same time Henry Hennell, of Apothecaries' Hall, had really effected the synthesis of alcohol—that is to say, had synthesised this compound in the same sense that Wöhler had synthesised urea. The history is soon told. In 1826 Hennell (through Brande) communicated a paper to the Royal Society which appears in the *Philosophical Transactions* for that year ("On the Mutual Action of Sulphuric Acid and Alcohol, with Observations on the Composition and Properties of the Resulting Compound," *Phil. Trans.*, 1826, p. 240). In studying the compounds produced by the action of sulphuric acid on alcohol, and known as "oil of wine," he obtained sulphovinic acid, which had long been known, and gave fairly good analyses of this acid and of some of its salts, while expressing in the same paper very clear notions as to its chemical nature. Having satisfied himself that sulphovinic acid is a product of the action in question, he then proceeded to examine some sulphuric acid which had absorbed eighty times its volume of olefiant gas, and which had been placed at his disposal for this purpose by Michael Faraday. From this he also isolated sulphovinic acid. In another paper, communicated to the Royal Society in 1828 ("On the Mutual Action of Sulphuric Acid and Alcohol, and on the Nature of the Process by which Ether is formed," *Phil. Trans.*, 1828, p. 365), he proves quantitatively that when sulphovinic acid is distilled with sulphuric acid and water the whole of the alcohol and sulphuric acid which united to form the sulphovinic acid are recovered. In the same paper he shows that he had very clear views as to the process of etherification. Hennell's work appears to have been somewhat dimmed by the brilliancy of his contemporaries who were labouring in the same field; but it is not too much to claim for him, after the lapse of nearly seventy years, the position of one of the pioneers of chemical synthesis. Of course, in his time the synthesis was not complete, because he did not start from inorganic materials. The olefiant gas used by Faraday had been obtained from coal-gas or oil-gas. Moreover, in 1826-1828 alcohol was not generally regarded as a product of vital activity, and this is, no doubt, the reason why the discovery failed to produce the same excitement as the formation of urea. But the synthesis of alcohol from ethylene had, nevertheless, been accomplished, and this hydrocarbon occupied at that time precisely the same position as ammonium cyanate. The latter salt had not then been synthesised from inorganic materials, and the formation of urea, as Schorlemmer points out ("The Rise and Development of Organic Chemistry," p. 195), was also not a complete synthesis. The reputation of Wöhler, the illustrious friend and colleague of the more illustrious Liebig, will lose not a fraction of its brilliancy by the raising of this historical question. Science recognises no distinction of nationality, and the future historian of synthetical chemistry will not begrudge the small niche in the temple of Fame to which Hennell is entitled.

Like many other great discoveries in science, the artificial formation of natural products began, as in the case of alcohol and urea, with observations arising from experiments not primarily directed to this end. It was not till the theory of chemical structure had risen to the rank of a scientific guide that the more complicated syntheses were rendered possible by more exact methods. We justly credit structural chemistry with these triumphant achievements. In arriving at such results any defects in the theory of structure are put out of consideration, because —and this point must never be lost sight of—all doubt as to the possibility of this or that atomic grouping being stable is set aside at the outset by the actual occurrence of the compound in nature. The investigator starts with the best of all assurances. From the time of Wöhler and Hennel the course of discovery in this field has gone steadily on. The announcement of a new synthesis has ceased to produce that excitement which it did in the early days when the so-called "organic" compounds were regarded as products of special vital force. The interest among the uninitiated now rises in proportion to the technical value of the compound. The present list of 180 odd synthetical products comprises, among the latest discoveries, gentisin, the colouring-matter of the gentian root (*Gentiana lutea*), which has been prepared by Kostanecki and Tambor, and caffeine, synthesised by Emil Fischer and Lorenz Ach, starting from dimethylurea and malonic acid.

I have allowed myself no time for those prophetic flights of the imagination which writers on this subject generally indulge in. When we know more about the structure of highly complex molecules, such as starch and albumen, we shall probably be able to synthesise these compounds. It seems to me more important just at present to come to an understanding as to what is meant by an organic synthesis. There appears to be an impression among many chemists that a synthesis is only effected when a compound is built up from simpler molecules. If the simpler molecules can be formed directly from their elements, then the synthesis is considered to be complete. Thus urea is a complete synthetical product, because we can make hydrogen cyanide from its elements: from this we can prepare a cyanate, and finally urea. In dictionaries and text-books we find synthetical processes generally separated from modes of formation, and the latter in their turn kept distinct from methods of preparation. The distinction between formation and preparation is obviously a good one, because the latter has a practical significance for the investigator. But the experience gained in drawing up the tables of synthesised compounds, to which I have referred, has resulted in the conclusion that the terms "synthesis" and "mode of formation" have been either unnecessarily confused or kept distinct without sufficient reason, and that it is impossible now to draw a hard-and-fast line between them. Some recent writers, such, for example, as Dr. Karl Elbs, in his admirable work on this subject ("Die Synthetischen Darstellungsmethoden der Kohlenstoffverbindungen," Leipzig, 1889), have expanded the meaning of the word synthesis so as to comprise generally the building up of organic molecules by the combination of carbon with carbon, without reference to the circumstance whether the compound occurs as a natural product or not. But although this definition is sufficiently wide to cover the whole field of the production of carbon compounds from less complex molecules, it is in some respects too restricted, because it excludes such well known cases as the formation of hydrogen cyanide from its elements, or of urea from ammonium cyanate. I should not consider the discussion of a mere question of terminology of sufficient importance to occupy the attention of this Section were it not for a matter of principle, and that a principle of the very greatest importance, which I believe to be associated with a clear conception of chemical synthesis. The great interest of all work in this field arises from our being able, by laboratory processes, to obtain compounds which are also manufactured in Nature's laboratory—the living organism. It is in this direction that our science encroaches upon biology through physiology. Now, if we confine the notion of synthesis to the building up of molecules from simpler molecules or from atoms, we exclude one of Nature's methods of producing many of these very compounds which we claim to have synthesised. There can be no manner of doubt that a large proportion, if not a majority, of the natural products which have been prepared artificially are not synthesised by the animal or plant in the sense of building up at all. They are the results of the breaking down—of the degradation—of complex molecules into simpler ones. I urge, therefore, that if in the laboratory we can arrive at one of these products by decomposing a more complex molecule by means of suitable reagents, we have a perfect right to call this a synthesis, provided always that the more complex molecule, which gives us our compound, can be in its turn synthesised, by no matter how many steps, from its constituent atoms. Thus, oxalic acid has been directly synthesised from carbon dioxide by Kolbe and Drechsel by passing this gas over potassium or sodium amalgam heated to 360°. Whether the plant makes oxalic acid directly out of carbon dioxide we cannot at present state; if it does it certainly does not employ Kolbe and Drechsel's process. On the other hand, this acid may, for all that is known, exist in the plant as a product of degradation. Many more complex acids, such as citric and tartaric, break down into oxalic acid when fused with potash. Both citric and tartaric acids can now be completely synthesised; therefore the formation of oxalic acid from these by potash fusion is a true synthesis.

The illustration given will make clear the point which I am urging. The distinction between a synthesis and a mode of formation vanishes when we can obtain a compound by the breaking down of a more complex molecule in all those cases where the latter can be completely built up. If we do not expand the meaning of synthesis so as to comprise such cases we are simply shutting the door in Nature's face. It must be borne in mind that the actual yield of the compound furnished by the laboratory process does not come into consideration, because it may be generally asserted that in most cases the artificial processes are not the same as those which go on in the animal or plant. The information of real value to the physiologist which these syntheses give is the suggestion that such or such a compound may possibly result from the degradation of this or that antecedent compound, and not from a process of building up from simpler molecules.

THE BEARING OF CHEMICAL SYNTHESIS ON VITAL CHEMISTRY.

With these views—the outcome of structural chemistry —the chemist and physiologist may join hands and move fearlessly onwards towards the great mystery of vital chemistry. In considering the results of organic synthesis two questions always arise, as it were spontaneously: How does Nature produce these complicated molecules without the use of strong reagents and at ordinary temperatures? What bearing have our laboratory achievements on the mechanism of vitality? The light shed upon these questions by experimental investigation has as yet flickered only in fitful gleams. We are but dwellers in the outer gates, waiting for the guide who is to show us the bearing of modern research on the great problem which confronts alike the physicist, the chemist, and the biologist. The chemical processes that go on in the living organism are complex to an extent that is difficult to realise. Of the various compounds of animal or vegetable origin that have been produced synthetically, some are of the nature of waste products, resulting from metabolic degradation; others are the result of zymolytic action within the organism; and others, again, are secondary products arising from the action of associated Bacteria, the relationship between the Bacteria and their host being as yet imperfectly understood. The answer to the question how Nature produces complicated organic molecules will be much facilitated when the physiologist, by experiment and observation, shall have made possible a sound classification of these synthetical products based on their mode of origination in the organism,

The enlargement of the definition of organic synthesis which I have advocated has been rendered necessary by the consideration of certain questions which have arisen in connection with the present condition of chemical discovery in this field. What evidence is there that any one of the 180 compounds which have been prepared artificially is produced in the organism by a direct process of building up? Is not the opposite view quite as probable? May they not, from the simplest to the most complex, be products of the degradation of still more complex molecules? I venture to suggest—not without some temerity, lest our colleagues of Sections I and K should treat me as an intruder—that this view should be given a fair trial. I am aware that the opposite view, especially as regards plant assimilation, has long been held, and especially since 1870, when v. Baeyer advanced his celebrated theory of the formic aldehyd origin of carbohydrates. It is but natural to consider that the formation of a complex molecule is the result of a building-up process. It must be remembered, however, that in the living organism there is always present a compound or mixture, or whatever we like to call it, of a highly complex proteid nature, which, although at present indefinite from the purely chemical point of view, is the essence of the vitality. Of course I refer to what biologists have called protoplasm. Moreover, it is perhaps necessary to state what is really nothing more than a truism, viz., that protoplasm is present in and forms a part of the organism from the very beginning of its existence—from the germ to the adult, and onwards to the end of life. Any special chemical properties pertaining to protoplasm are inseparable from the animal or plant until that period arrives which Kekulé has hinted at when we shall be able to "build up the formative elements of living organisms" in the laboratory (*Nature*, xviii., 212). But here I am afraid I am allowing the imagination to take a flight which I told you a few minutes ago that time would not admit of.

The view that requires pushing forward into a more prominent position than it has hitherto occupied is that all the chemical transformations in the organism—at any rate all the primary changes—are made possible only by the antecedent combination of the substances concerned with living protoplasmic materials. The carbon dioxide, water, &c., which the plant absorbs, must have formed a compound or compounds with the protoplasmic material of the chloroplasts before starch, or sugar, or cellulose can be prepared. There is, on this view, no such process as *the direct combination* of dead molecules to build up a complex substance. Everything must pass through the vital mill. The protoplasmic molecule is vastly more complex than any of the compounds which we have hitherto succeeded in synthesising. It might take up and form new and unstable compounds with carbon dioxide or formic aldehyd, or sugar, or anything else, and our present methods of investigation would fail to reveal the process. If this previous combination and, so to speak, vitalisation of dead matter actually occurs, the appearance of starch as the first visible product of assimilation, as taught by Sachs, or the formation of a 12-carbon-atom sugar as the first carbohydrate, as shown by the recent researches of Horace Brown and G. H. Morris, is no longer matter for wonderment. The chemical equations given in physiological works are too purely chemical; the physiologists have, I am afraid, credited the chemists with too much knowledge—it would appear as though their intimate familiarity with vital processes had led them to undervalue the importance of their prime agent. In giving expression to these thoughts I cannot but feel that I am treating you to the strange spectacle of a chemist pleading from the physiologists for a little more vitality in the chemical functions of living organisms. The future development of vital chemistry rests, however, with the chemist and physiologist conjointly; the isolation, identification, and analysis of the products of vital activity, which has hitherto been the task of the chemist, is only the preliminary work of physiological chemistry leading up to chemical physiology.

(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 August 31st, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 10th, 1895.

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 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 Aug. 1st to Aug. 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 two were recorded as "clear, but dull;" the remainder being clear, bright, and well filtered.

The rainfall in the Thames Valley during August has been close upon the average. The actual amount is 2·28 inches, and the twenty-five years' mean is 2·24, showing an excess of 0·04 inch. By far the greater part of the rain fell in the first part of the month, only 0·36 inch having fallen since the 14th.

The Thames-derived waters still maintain the high degree of purity we had to record in the reports for June and July. Compared with the waters in July, there is scarcely any analytical difference. Compared with the waters for the corresponding month last year, there is an appreciable diminution in some of the constituents, as seen by the following table.

Our bacteriological examinations of the unfiltered Thames waters and of the clear water drawn from the general wells of the Water Companies show that the microbial life in the river is diminishing, whilst the Com-

Comparison of the Averages of the Five Thames-derived Supplies for the Months of August, 1894 *and* 1895.

	Common Salt.	Nitric Acid.	Hardness.	Oxygen. reqd.	Organic Carbon.	Organic Carbon.	Colour.
	Per gall.	Per gall.	Degrees.	Per gall.	Per gall.	Per gall.	Br'n : Blue.
	Means.	Means.	Means.	Means.	Means.	Maxima.	Means.
Aug., 1894	2·077	0·589	12·30	0·048	0·105	0·138	21·5 : 20
1895	1·994	0·740	13·09	0·039	0·093	0·108	11·7 : 20

panies' filters continue to work with efficiency. The unfiltered waters contained an average of 1720, and the clear filtered waters flowing into the pipes contained an average of 34 bacteria per c.c. These were all harmless river microbes.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

CORRESPONDENCE.

DISINFECTANTS.

To the Editor of the Chemical News.

Sir,—In your reviewer's notice of my book on "Disinfectants" he adds to the following quotation from p. 11 the words which I have italicised:—"A large number of processes have endeavoured to recover the phosphate *of sewage* by using the sludge as a fertiliser, but they have all met with little commercial success;" and then proceeds to say, this statement "we must pronounce as utterly mistaken." His own additional words are those which have led him to express this opinion, as the context shows the phosphate referred to is not the phosphate of sewage, but the phosphate of animal charcoal, the whole of this section being devoted to remarks on the use of this material for purifying and deodorant purposes.—I am, &c.,

Samuel Rideal.

Chemical Laboratory,
28, Victoria St., Westminster, S.W.,
September 2, 1895.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) at the Ipswich Meeting of the British Association:—

President—Prof. R. Meldola, F.R.S., Foreign Sec. C.S.

Vice-Presidents—Prof. P. P. Bedson, D.Sc.; Prof. H. B. Dixon, M.A., F.R.S.; Prof. E. Frankland, D.C.L., F.R.S.; Dr. J. H. Gladstone, Ph.D., F.R.S.; Prof. Ira Remsen, Ph.D.; Sir H. E. Roscoe, D.C.L., F.R.S.

Secretaries—E. Herbert Fison, C. A. Kohn. Arthur Harden (Recorder), J. W. Rodger.

Committee—Prof. H. E. Armstrong, F.R.S.; R. N. Atkinson; J. Carter Bell; C. H. Bothamley; Prof. J. Campbell Brown; Prof. F. Clowes; T. Fairley; A. E. Fletcher; C. J. Fowler; Prof. Franchimont; A. G. Vernon Harcourt, F.R.S., Pres. C.S.; Prof. Liveing, F.R.S.; Prof. H. McLeod, F.R.S.; H. Forster Morley; Manning Prentice; Lord Rayleigh, Sec. R.S.; A. Richardson; Prof. A. Smithells; J. Spiller; Prof. R. Warington, F.R.S.; W. Marshall Watts; Prof. W. Carleton Williams; G. Young.

The Papers brought before the Section were as follows:—

President's Address.

Sir H. E. Roscoe and *Arthur Harden*—A New View of the Genesis of Dalton's Atomic Theory, derived from Original Manuscripts.

Dr. J. H. Gladstone—Report of the Committee on the Teaching of Science in Elementary Schools.

G. J. Fowler—The Action of Nitric Oxide on some Metallic Salts.

Prof. F. Clowes—The Respirability of Air in which a Candle Flame has Burnt until it is Extinguished.

D. J. P. Berridge—The Action of Light upon the Soluble Metallic Iodides in presence of Cellulose.

Dr. C. A. Kohn—Report of the Committee on Quantitative Analysis by means of Electrolysis.

Sir H. E. Roscoe—Report of the Committee Appointed to Prepare a New Series of Wave-length Tables of the Spectra of the Elements.

A Discussion was held in conjunction with Section K (Botany) on the Relation of Agriculture to Science. The Discussion was introduced by the following papers:—

Prof. R. Warington—How Shall Agriculture best obtain Help from Science?

T. Hendrick—Agriculture and Science.

M. J. R. Dunstan—The Application of Science to Agriculture.

T. B. Wood—Work at the Experimental Plots in Norfolk and Suffolk.

Report of the Committee on the Preparation of Pure Haloids.

Report of the Committee on the Bibliography of Spectroscopy.

Dr. H. W. Vogel—Some Remarks on Orthochromatic Photography.

C. H. Bothamley—The Sensitising Action of Dyes on Gelatino-bromide Plates.

Report of the Committee on the Action of Light on Dyed Colours.

Dr. J. J. Sudborough—Some Stilbene Derivatives.

Dr. J. J. Sudborough—Note on the Constitution of Camphoric Acid.

Dr. M. Wildermann—Experimental Proof of Van 't Hoff's Constant, of Dalton's Law, &c., for very Dilute Solutions.

H. J. H. Fenton—The Formation and Properties of a New Organic Acid.

Dr. M. Wildermann—On the Velocity of Reaction before perfect Equilibrium takes place.

C. F. Cross and *C. Smith*—The Chemical History of the Barley Plant.

Joint Sitting of Sections A and B:—

Lord Rayleigh, Sec. R.S.—On the Refraction and Viscosity of Argon and Helium.

Dr. J. H. Gladstone, F.R.S.—On Specific Refraction and the Periodic Law, with reference to Argon and other Elements.

A Discussion "On the Evidence to be gathered as to the Simple or Compound Character of a Gas, from the Constitution of its Spectrum." The Discussion was opened by Prof. A. Schuster, F.R.S. Lord Rayleigh, Sec. R.S., and Prof. Runge and others joined in the Discussion, and Dr. Johnstone Stoney, F.R.S., read a paper on "The Interpretation of Spectra."

The Chemical Laboratory of Wiesbaden.—In the Summer Term, 1895, there were fifty-four students on the books. Of these, thirty-four were from Germany, four from England, four from Norway, two from Austro-Hungary, two from Holland, two from Belgium, two from Australia; also one from each of the following countries—Switzerland, Italy, Russia, and United States of America. In place of Professor Borgmann, deceased in April, Dr. L. Grünhut has been nominated as teacher of chemical technology. Other changes in the teachers have not taken place. The assistants in the instruction laboratory were three in number, in the Versuchsstationen (private laboratories) twenty. The next Winter Term begins the 15th of October. The Versuchsstation has been appointed as one of the institutions where chemists can receive the practical instruction in the analysis of food necessary for the admission to the examination for food analysts. 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.

The People's Palace.—In the South Kensington Examinations last year, the Day School obtained 2 Honours First, 4 Honours Second; 56 Adv. First, 131 Adv. Second; 455 Elementary Passes. Evening Classes, 4 Hon. First, 7 Hon. Second; 23 Adv. First, 139 Adv. Second; 200 Elementary Passes in science subjects. In addition to these, 11 First, 68 Second, and 47 Elementary Passes were obtained by the Day School in Mathematics, and 3 First 26 Second, and 7 Passes by the Evening Class students. Among the latter are included 10 students who were successful in the Department Examination in Conic Sections and Differential and Integral Calculus. In Art, the Day School obtained 121 First and 138 Second, and the Evening Classes 2 Excellent, 104 First, and 135 Second. In the Evening Classes successes were likewise obtained in the City and Guilds Examination and in those of the University of London. Out of 50 London County Council Evening Exhibitions awarded to students from various polytechnics, 21 were obtained by those from the People's Palace. The chemical laboratory has been entirely re-fitted through the generosity of the Drapers' Company.

Charterhouse Science and Art Schools and Literary Institute.—The Winter Session will commence on Saturday, September 28th, under the Presidency of the Rev. Henry Swann, M.A. During the late Session upwards of 1200 students, mostly elementary teachers, availed themselves of the privileges offered by this Institution. Of this number, 682 presented themselves for examination, and were successful in obtaining a large number of certificates awarded by the Science and Art Department of South Kensington. Several students prepared for the Lond. B.Sc. (Int.) Examination. Instruction of a practical character is given in most of the sciences at a very nominal fee, whilst in Art at an equally low rate students, under the direction of competent instructors, can be advanced in their studies. Those who have leisure can, at a very moderate charge, attend the Day Classes in Art. Day Classes will be held to prepare candidates for Matriculation (Lond.), the Clerical, Medical (including Dental), and other Examinations. Students who aim at becoming proficient in Chemistry (Organic and Inorganic) have the opportunity of working in a well-fitted laboratory. Aspirants for university honours can, at a very small expense, be assisted in their studies. Classes for Matriculation, Microscopy, Latin, Greek, French, German, Shorthand, and Music are taught by well-qualified teachers. Opportunities for the study of photography, &c., are to be continued this Session. Full particulars of the classes are to be obtained from C. Smith, Organising Secretary. An organised Day Science School for Boys and Girls is now in full operation. A special course of lectures on Agriculture, Hygiene, and Physiology is arranged for the coming Session.

Battersea Polytechnic Institute.—This Institute has been built and equipped at a cost of over £55,000, the greater part of which has been raised by voluntary subscriptions. It is at present in possession of a fixed endowment of £2500 per year from the City Parochial Foundation. The London County Council also contributes an annual sum, estimated to amount to about £2500. It is under the direction of a Governing Body consisting of representatives of the South London Polytechnics Committee, the City Parochial Foundation, the London County Council, and the London School Board. The principal work of the Institute is the provision of Evening Classes for both sexes in all subjects of Technology, Pure and Applied Science, Art, Commerce, Domestic Economy, and Music; but it also provides a Technical and Science Day School for Boys and Girls, a Training School of Domestic Economy, and a Domestic Economy School for Girls. During the last Session, 1894-95, the Evening Classes were attended by over 2930 persons, while 160 students were in regular attendance at the Day Schools. The Institute is provided with well equipped workshops, and also with laboratories for Engineering and Mechanics, Electrical Engineering, Physics, Chemistry, and Natural Science. Classes will commence on September 23rd.

THE CHEMICAL NEWS.

Vol. LXXII., No. 1870.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Ipswich, 1895.

By Prof. RAPHAEL MELDOLA, F.R.S., F.I.C., For. Sec. C.S., President of the Section.

(Concluded from p. 148).

Protoplasmic Theory of Vital Synthesis.

The supposition that chemical synthesis in the organism is the result of the combination of highly complex molecules with simpler molecules, and that the unstable compounds thus formed then undergo decomposition with the formation of new products, may be provisionally called the protoplasmic theory of vital synthesis. From this standpoint many of the prevailing doctrines will have to be inverted, and the formation of the more complex molecules will be considered to precede the synthesis of the less complex. It may be urged that this view simply throws back the process of vital synthesis one stage, and leaves the question of the origin of the most complex molecules still unexplained. I grant this at once; but in doing so I am simply acknowledging that we have not yet solved the enigma of life. We are in precisely the same position as is the biologist with respect to abiogenesis, or the so-called "spontaneous generation." To avoid possible misconception let me here state that the protoplasmic theory in no way necessitates the assumption of a special "vital force." All that is claimed is a peculiar, and at present to us mysterious, power of forming high-grade chemical combinations with appropriate molecules. It is not altogether absurd to suppose that this power is a special property of nitrogen in certain forms of combination. The theory is but an extension of the views of Kühne, Hoppe-Seyler, and others, respecting the mode of action of enzymes. Neither is the view of the degradational origin of synthetical products in any way new.[*] I merely have thought it desirable to push it to its extreme limit in order that chemists may realise that there is a special chemistry of protoplasmic action, while the physiologists may exercise more caution in representing vital chemical transformations by equations which are in many cases purely hypothetical, or are based on laboratory experiments which do not run parallel with the natural process. The chemical transformations which go on in the living organism are thus referred back to a peculiarity of protoplasmic matter, the explanation of which is bound up with the inner mechanism of the process of assimilation. If, as the protoplasmic theory implies, there must be combination of living protoplasm with appropriate compounds before synthesis is possible, then the problem resolves itself into a determination of the conditions which render such combination possible,—*i. e.*, the conditions of assimilation. It may be that here also light will come from the stereochemical hypothesis. The first step was taken when Pasteur found that organised ferments had the power of discriminating between physical isomerides; a similar selective power has been shown to reside in enzymes by the researches of Emil Fischer and his coadjutors. Fischer has quite recently expressed the view that the synthesis of sugars in the plant is preceded by the formation of a compound of carbon dioxide, or of formic aldehyd, with the protoplasmic material of the chloroplast, and similar views have been enunciated by Stohmann. The question has further been raised by van 't Hoff, as well as by Fischer, whether a stereochemical relationship between the living and dead compounds entering into combination is not an absolutely essential condition of all assimilation. The settlement of this question cannot but lead us onwards one stage towards the solution of the mystery that still surrounds the chemisty of the living organism.

Recent Discoveries of Gaseous Elements.

The past year has been such an eventful one in the way of startling discoveries that I must ask indulgence for trespassing a little further upon the time of the Section. It was only last year, at the Oxford meeting of the British Association, that Lord Rayleigh and Prof. Ramsay announced the discovery of a gaseous constituent of the atmosphere which had up to that time escaped detection. The complete justification of that announcement is now before the world in the paper recently published in the *Philosophical Transactions of the Royal Society*. The history of this brilliant piece of work is too recent to require much recapitulation. I need only remind you how, as the result of many years' patient determinations of the density of the gases oxygen and nitrogen, Lord Rayleigh established the fact that atmospheric nitrogen was heavier than nitrogen from chemical sources, and was then led to suspect the existence of a heavier gas in the atmosphere. He set to work to isolate this substance, and succeeded in doing so by the method of Cavendish. In the meantime Prof. Ramsay, quite independently, isolated the gas by removing the nitrogen by means of red-hot magnesium, and the two investigators, then combining their labours, followed up the subject, and have given us a memoir which will go down to posterity among the greatest achievements of an age renowned for its scientific activity.

The case in favour of argon being an element seems to be now settled by the discovery that the molecule of the gas is monatomic, as well as by the distinctness of its electric spark spectrum. The suggestion put forward soon after the discovery was announced, that the gas was an oxide of nitrogen, must have been made in complete ignorance of the methods by which it was prepared. The possibility of its being N_3 has been considered by the discoverers and rejected on very good grounds. Moreover, Peratoner and Oddo have been recently making some experiments in the laboratory of the University of Palermo with the object of examining the products of the electrolysis of hydrazoic acid and its salts. They obtained only ordinary nitrogen, not argon, and have come to the conclusion that the anhydride $N_3.N_3$ is incapable of existence, and that no allotropic form of nitrogen is given off. It has been urged that the physical evidence in support of the monatomic nature of the argon molecule, viz., the ratio of the specific heats, is capable of another interpretation—that argon is, in fact, an element of such extraordinary energy that its atoms cannot be separated, but are bound together as a rigid system which transmits the vibrational energy of a sound-wave as motion of translation only. If this be the state of affairs we must look to the physicists for more light. So far as chemistry is concerned, this conception introduces an entirely new set of ideas, and raises the question of the monatomic character of the mercury molecule which is in the same category with respect to the physical evidence. It seems unreasonable to invoke a special power of atomic linkage to explain the monatomic character of argon, and to refuse such a power in the case of other monatomic molecules like mercury or cadmium. The chemical inertness of argon has been referred also to this same power of self-combination of its atoms. If this explana-

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[*] See, *e.g.*, Vines's "Lectures on the Physiology of Plants," pp. 145, 218, 227, 233, and 234. Practically all the great classes of synthetical products are regarded as the results of the destructive metabolism of protoplasm. A special plea for protoplasmic action has also been urged, from the biological side, by W. T. Thiselton-Dyer, *Journ. Chem. Soc.*, 1893; *Trans.*, pp. 680, 681.

tion be adopted it carries with it the admission that those elements of which the atoms composing the molecule are the more easily dissociated should be the more chemically active. The reverse appears to be the case if we bear in mind Victor Meyer's researches on the dissociation of the halogens, which prove that under the influence of heat the least active element, iodine, is the most easily dissociated. On the whole, the attempts to make out that argon is polyatomic by such forced hypotheses cannot at present be considered to have been successful, and the contention of the discoverers that its molecule is monatomic must be accepted as established.

In searching for a natural source of combined argon Professor Ramsay was led to examine the gases contained in certain uranium and other minerals, and by steps which are now well known he has been able to isolate helium, a gas which was discovered by means of the spectroscope in the solar chromosphere, during the eclipse of 1868, by Professors Norman Lockyer and E. Frankland. In his Address to the British Association in 1872 (*Reports*, 1872, p. lxxiv) the late Dr. W. B. Carpenter said:—

"But when Frankland and Lockyer, seeing in the spectrum of the yellow solar prominences a certain bright line not identifiable with that of any known terrestrial flame, attribute this to a hypothetical new substance which they propose to call helium, it is obvious that their assumption rests on a far less secure foundation, until it shall have received that verification which, in the case of Mr. Crookes's researches on thallium, was afforded by the actual discovery of the new metal, whose presence had been indicated to him by a line in the spectrum not attributable to any substance then known."

It must be as gratifying to Professors Lockyer and Frankland as it is to the chemical world at large to know that helium may now be removed from the category of solar myths and enrolled among the elements of terrestrial matter. The sources, mode of isolation, and properties of this gas have been described in the papers recently published by Professor Ramsay and his colleagues. Not the least interesting fact is the occurrence of helium and argon in meteoric iron from Virginia, as announced by Professor Ramsay in July (*Nature*, vol. lii., p. 224). Like argon, helium is monatomic and chemically inert, so far as the present evidence goes. The conditions under which this element exists in clèveite, uraninite, and the other minerals, have yet to be determined.

Taking a general survey of the results thus far obtained, it seems that two representatives of a new group of monatomic elements characterised by chemical inertness have been brought to light. Their inertness obviously interposes great difficulties in the way of their further study from the chemical side; the future development of our knowledge of these elements may be looked for from the physicist and spectroscopist. Prof. Ramsay has not yet succeeded in effecting a combination between argon or helium and any of the other chemical elements. M. Moissan finds that fluorine is without action on argon. M. Berthelot claims to have brought about a combination of argon with carbon disulphide and mercury, and with "the elements of benzene, . . . with the help of mercury," under the influence of the silent electric discharge. Some experiments which I made last spring with Mr. R. J. Strutt with argon and moist acetylene submitted to the electric discharge, both silent and disruptive, gave very little hope of a combination between argon and carbon being possible by this means. The coincidence of the helium yellow line with the D_3 line of the solar chromosphere has been challenged, but the recent accurate measurements of the wave-length of the chromospheric line by Prof. G. E. Hale, and of the line of terrestrial helium by Mr. Crookes, leave no doubt as to their identity. Both the solar and terrestrial lines have now been shown to be double. The isolation of helium has not only furnished another link proving community of matter, and, by inference, of origin between the earth and sun, but an extension of the work by Professor Norman Lockyer, M. Deslandres, and Mr. Crookes has resulted in the most interesting discovery that a large number of the lines in the chromospheric spectrum, as well as in certain stellar spectra, which had up to the present time found no counterparts in the spectra of terrestrial elements, can now be accounted for by the spectra of gases contained with helium in these rare minerals. The question now confronts us, Are these gases members of the same monatomic inert group as argon and helium? Whether, and by what mechanism, a monatomic gas can give a complicated spectrum is a physical question of supreme interest to chemists, and I hope that a discussion of this subject with our colleagues of Section A will be held during the present meeting. That mercury is capable under different conditions of giving a series of highly complex spectra can be seen from the memoir by J. M. Eder and E. Valenta, presented to the Imperial Academy of Sciences of Vienna, in July, 1894. With respect to the position of argon and helium in the periodic system of chemical elements, it is, as Professor Ramsay points out, premature to speculate until we are quite sure that these gases are homogeneous. It is possible that they may be mixtures of monatomic gases, and in fact the spectroscope has already given an indication that they contain some constituent in common. The question whether these gases are mixtures or not presses for an immediate answer. I will venture to suggest that an attack should be made by the method of diffusion. If argon or helium were allowed to diffuse fractionally through a long porous plug into an exhausted vessel there might be some separation into gases of different densities, and showing modifications in their spectra, on the assumption that we are dealing with mixtures composed of molecules of different weights.

THE REFRACTION AND VISCOSITY OF ARGON AND HELIUM.*

By The Right Hon. Lord RAYLEIGH, Sec.R.S.

As compared with dry air, the refraction ($\mu - 1$) of argon is 0·961 and that of helium (prepared by Prof. Ramsay) is as low as 0·146.

Dry air being again taken as the standard, the viscosity of argon is 1·21, and that of helium is 0·96.

ON THE

PRESENCE OF ARGON AND OF HELIUM IN CERTAIN MINERAL WATERS.

By Dr. C. H. BOUCHARD.

The escape of very fine gaseous bubbles occurring in certain sulphuretted waters from the Pyrenees has been observed long ago. It begins a short time after such water has been drawn, and continues for a time variable according to the springs, sometimes for hours. In these waters, rendered slightly alkaline by sodium sulphide and silicate, these gases can neither be oxygen nor carbonic acid. It has been admitted, doubtless in consequence of the negative character of this substance, that it can only be nitrogen.

Spanish physicians have especially fixed their attention on this feature. They have named the waters which evolve nitrogen "azoades." They are found on the Spanish slope of the Pyrenees at Panticosa. On the French slope they are found at several stations, especially at the medicinal springs of Bagnères-de-Bigorre and at Cauterets, at the source of the Raillière.

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* Read before the British Association (Section B), Ipswich Meeting, 1895.

Other springs in the Pyrenees which do not show any effervescence allow at intervals the escape of large bubbles of gas which are also considered as nitrogen.

During a recent stay at Cauterets, I had the curiosity to collect information of the gases which occasion these two kinds of phenomena. I succeeded in collecting somewhat considerable quantities of these gases at the point of issue, before any contact with the atmosphere, at the source of the Raillière and at two of the springs which feed the source of the Bois.

I have, thanks to the kindness of M. du Perron, the director of the waters, been enabled to examine the gas extracted from the bottled water of the Raillière, obtained by means of the mercurial pump, and also by ebullition.

Our colleague, M. Troost, who was present at my first experiments, has kindly offered his assistance for the determination of the physical and chemical characters of these gases, and the results which I now communicate to the Academy have been obtained with his assistance and under his direction.

These gases, when dried over potassa and phosphoric anhydride, have the characters of nitrogen; if heated to redness over magnesium wire for forty-eight hours, they lose their original volume. At the same time the wire is covered with a yellow layer, which on exposure to the air becomes white and evolves ammonia.

If the gas thus reduced is introduced into Plücker tubes with magnesium wires, and if under a low pressure, and with an effluve capable of heating the magnesium sufficiently, we exhaust the last traces of nitrogen (the spectrum of which disappears), we observe that the residual gases from the different springs are not identical.

The gases collected at the spring of the Raillière or extracted by boiling the waters of the same spring have given the characteristic rays of argon as well as those of helium.

The gases collected at the springs of the source of the Bois have all given both the characteristic rays of helium.

The gases collected at one of the two springs of the Bois (the one having the lowest temperature) lead us to suspect, on account of the abundance of rays in the red and the orange, that they contain some other element along with helium.

In our present ignorance of the physiological properties of argon and helium, we may ask if there is any relation between the medicinal properties of the waters of the Pyrenees and the composition of the gases which they evolve. The fact seems to me improbable.

The idea proposed twenty-five years ago by the Spanish physicians that the "azoades" owe their virtues to the nitrogen which they evolve has been abandoned. May these virtues, in default of nitrogen, depend on gases which are chemically less active than nitrogen, and which are present in the waters in a smaller proportion? It is, strictly speaking, possible; but the question ought not even to be raised if it is demonstrated that these gases are found also, and in analogous proportions, in the waters which flow or remain on the surface of the earth, and which serve us for dietetic purposes.

We are not absolutely certain concerning the origin of all the gases of mineral waters, and it may be that those with which we are concerned have their origin in the air carried down into deeper regions by the superficial waters. These waters, after being alkalised by a sulphide, may re-ascend towards the surface necessarily deprived of oxygen and carbonic acid, and containing merely nitrogen and argon. Nevertheless, it seems at present that to the possible atmospheric origin of a part of the argon, and perhaps of the helium, there must be added some subterranean action, since if one of our springs contains both gases, another contains only helium, and a third contains along with helium something which is not argon.

The investigation which we have just made involves a research into the composition of the gases contained in waters on the surface of the earth. The results of this study, which is in progress, will be communicated to the Academy.—*Comptes Rendus*, cxxi., p. 392.

THE COMBINATION OF MAGNESIUM WITH ARGON AND HELIUM.

By L. TROOST and L. OUVRARD.

If it is requisite to examine if there exists argon or helium in nitrogen gas it is not indispensable to pass the mixture over magnesium heated to redness or over lithium heated to dull redness in order to absorb the larger part of the nitrogen before causing the effluve to act on the gaseous mixture. The use of Plücker tubes with magnesium wire and a Rhumkorff coil fitted with a Marcel Deprez interrupter, enables us to act at once upon a mixture containing only very small proportions of argon and helium.

This we have observed especially with the gases collected by Dr. Bouchard at the spring at the source of the Raillière, and at those of the Bois (at Cauterets).

We may at once introduce the dried gases into Plücker tubes with magnesium wires, and pass into them strong effluves. The nitrogen is only slowly absorbed at first, but when the pressure is sufficiently decreased the temperature of the magnesium wires rises sufficiently to occasion a commencement of evaporation which gives a metallic deposit in the state of a mirror on the glass of the tube around the wires. The combination of nitrogen with the magnesium vapour, which takes place with extreme rapidity, and the spectrum of nitrogen disappears. After this moment, the red rays characteristic of argon may be distinctly seen, or the red ray, D_4, and the other rays characteristic of helium.

The brightness of these spectra may be increased by introducing at intervals fresh quantities of the gas into the Plücker tube, fitted with a good glass cock, and passing in again strong effluves.

If we continue the passage of strong effluves for some hours, the luminous intensity of the rays diminishes by degrees, and a complete vacuum is formed. The argon and helium which do not seem to combine in a sensible manner with magnesium heated to redness, combine with this metal, or rather with its vapour, under the prolonged influence of powerful effluves.

As Berthelot as pointed out, the use of the effluve constitutes the most effective procedure to determine these combinations.

In argon, platinum presents phenomena of evaporation and combination analogous to those presented by magnesium.—*Comptes Rendus*, cxxi., p. 394.

SOME REACTIONS OF FORMALDEHYD.

By T. H. LEE.

Formalin (40 per cent formaldehyd) from Schering, of Berlin, was taken.

Permanganate of potassium immediately reduced. The formaldehyd fully oxidised to CO_2 and water. Ferric chloride solution (hot) is somewhat deepened in colour when formaldehyd is added. On allowing to cool, then re-heating and adding a little ammonium hydrate, a bulky red precipitate of basic ferric formate appears.

Ammoniacal silver solution appears to be reduced in two stages, viz.:—

1. $Ag_2O + H.COH = Ag_2 + H.CO_2H$. In this stage the silver falls in the specular form.
2. $Ag_2O + H.CO_2H = Ag_2 + H_2O + CO_2$. In this stage the silver falls in a pulverulent form.

A hot solution of potassium ferricyanide was made ammoniacal and a little formalin and sulphate of copper solution added. A brown precipitate immediately appeared. The same reagents minus the formalin gave a fine green solution. This I regard as evidence of the reduction of ferricyanide to ferrocyanide.

Hot Fehling's solution is rapidly reduced by formaldehyd.

Ammoniacal copper sulphate *per se* is not reduced. Mercuric chloride is not reduced.

Alkaline mercuro-potassium iodide is immediately reduced to metal in the cold.

Edgcumbe Villa, Clevedon.

ON THE REFRACTION AND DISPERSION OF LIQUID OXYGEN.*

By Professors LIVEING and DEWAR.

In August, 1892, we published in the *Philosophical Magazine* (vol. xxxiv., p. 208) a measure of the refractive index of liquid oxygen at its boiling-point for the yellow sodium rays, made by means of a prism. In the following year (vol. xxxvi., p. 330) we published a measure of the same quantity made by a different method. For the reasons stated, we could only obtain measures more or less approximate to the truth. Since then we have made several attempts, but hitherto in vain, to make hollow prisms with vacuous jackets, in which the liquid oxygen could be kept in a tranquil state while the observations were going on. We have also attempted unsuccessfully other methods of taking the measures.

The chief difficulties which we encountered in making our former measures arose from the irregularities and striations of the glass vessels, and from the continual ebullition of the liquid oxygen. These difficulties have now been to a great extent obviated. We have come back to the method we used in 1893, which we then described as the method of MM. Terquem and Trannin, but which had previously been suggested by Prof. E. Wiedemann (*Archives de Genève*, li., p. 340, 1874). However, for the cylindrical vessel before used we substituted a globular vessel having the inside of its vacuous jacket silvered all over except a narrow vertical strip about 4 m.m. wide, which was left unsilvered to allow of the passage of light. This vessel was used, exactly as the cylindrical vessel had been used in the former experiments, as a lens by which an image of a source of light was thrown on to the slit of a spectroscope. The pair of glass plates, separated by a thin stratum of air and fixed to a rod which was the prolongation of the vertical axis of a theodolite, were arranged at about the centre of the globe. The oxygen in the globe was very tranquil, and the silvering cut off all light which did not pass nearly centrally through the globe. The result was that the light of the rays observed was cut off, when the glass plates were turned through the proper angle, much more sharply than before, and the measures are so much more trustworthy.

We found the spark between cadmium electrodes a convenient source of light, both because the rays are bright, and because they are dispersed through a considerable range in the visible spectrum, and it was possible to watch their extinction one after another as the glass plates were slowly turned. Even with this arrangement the extinction of the rays when liquid oxygen was in the globe was not quite so sharp as when the experiment was made with alcohol. This was probably due to the scattered light from the bubbles in the oxygen, and was more troublesome in regard to the brightest rays.

We obtained, as the mean of several observations, for the blue ray of cadmium, λ 4416, $\mu = 1{\cdot}2249$; for the red ray, λ 6438, $\mu = 1{\cdot}2211$; for the green ray of thallium, λ 535, $\mu = 1{\cdot}2219$. Also, by using a flame, we obtained for the red ray of lithium, λ 6705, $\mu = 1{\cdot}2210$, and for the yellow rays of sodium, λ 5892, $\mu = 1{\cdot}2214$,

The last figure is less than we had found in 1892 by the prism method, which was 1·2236, and still less than than that found in 1893, which was 1·226. It is also less than thst recently found by Olszewski and Witrowski, (*Bull. de l'Acad. de Cracovie*, July, 1894, p. 246), which was between 1·2222 and 1·2235. The values we have now found for the refractive indices corresponding to the red ray of lithium and the green ray of thallium are also less than those found by Olszewski and Witrowski, which were about 1·2213 and 1·2235 respectively. We think, however, that our measures for the red and blue rays of cadmium are better than those made for the thallium and sodium rays.

These give, for the mean green, μ nearly equal to 1·222, and, taking the density of oxygen at its boiling-point as 1·137, the refraction-constant by Gladstone's formula—

$$\frac{\mu - 1}{d} = {\cdot}0{\cdot}1953,$$

and by Lorenz's formula—

$$\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0{\cdot}1242.$$

Taking Regnault's value for the density of oxygen gas at 0° and 76 c.m., viz., 0·00143, and Mascart's value for the mean refractive index, viz., 1·000271, we find for gaseous oxygen the refraction-constant—

$$\frac{\mu - 1}{d} = 0{\cdot}18947,$$

and—

$$\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0{\cdot}12631.$$

It will be seen that this last is nearly equal to the refraction-constant as above determined for the liquid,

In Mascart's paper "Sur la Refraction des Gaz" (*Annales l'Ecole Normale Expérimental*, 1876) some observations on the "Dispersion of Oxygen and other Gases" were given, which enable a comparison to be made between this property in the gaseous and liquid states. Taking Cauchy's formula—

$$n - 1 = a\left(1 + \frac{b}{\lambda^2}\right)$$

then—

$$\frac{n' - n}{n + 1} = b\,\frac{\frac{1}{\lambda^2} - \frac{1}{\lambda^2}}{1 + \frac{b}{\lambda^2}}$$

From this b is calculated by Mascart, and is called the Coefficient of Dispersion. The blue and red cadmium lines represent the extremest difference of wave-lengths employed. This gave for oxygen the maximum and minimum values 0·0049 and 0·0078, and mean value 0·0064 for the Constant of Dispersion. Taking the values for the liquid state given above, the value of b becomes 0·0064. It seems, therefore, that the Dispersion Constant in the liquid state is identical with that of the gas.

The Examinational System.—At the recent Congress of the Society of Chemical Industry, held at Leeds, July 31st to August 2nd, Dr. T. E. Thorpe, F.R.S., in his Presidential Address, expressed the timely opinion that we need institutions of research where young men, no longer haunted by the spectra of the ever-threatening examination, may find time and scope to practise their minds in real investigations and try their powers in attempts to promote Science and extend its domain.

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* From the *Philosophical Magazine* for September.

CALAVERITE FROM CRIPPLE CREEK, COLORADO.*

By W. F. HILLEBRAND.

The occurrence of tellurium in the ores of the mining district of Cripple Creek, Colorado, has been known from an early day in the as yet brief industrial history of that region. That it was, in part at least, associated with gold was likewise known from the observance of a crystallised gold-tellurium mineral. Although the ores of the district are chiefly gold carriers, they contain also a little silver, and since recognised silver minerals had not been observed, or at most only in minute amount, it seemed probable that the silver was associated with the gold in the tellurium compound. Indeed, Mr. R. Pearce, of Denver, came to the conclusion, from his examination (*Proc. Colo. Sci. Soc.*, Jan. 8 and April 5, 1894) of certain ore concentrates, that this mineral was sylvanite. It is, however, of very sparing occurrence, so that it was only by dint of much effort that material in sufficient purity for decisive tests was obtained by Prof. R. A. F. Penrose, jun., who transferred it to me for chemical examination. The material was derived from three different mines in order to ascertain whether it was of constant or varying composition, or, in fact, whether there might not be more than one specific telluride. That the composition does vary within narrow limits the analyses show, but there is no reason apparent for assuming more than one species.

The material from the Prince Albert mine, the first received, was with little trouble brought into an almost ideal condition of purity. It was in part apparently fairly well crystallised, but the measurements made by Prof. S. L. Penfield, of New Haven, are unfortunately not decisive as to the system of crystallisation, as shown by his notes at the close of this paper. The specific gravity of this material was 8·91 at 24° C., which becomes 9·00 when corrected for a small admixture of silico-ferruginous gangue of assumed specific gravity 2·70 (probably low). The other samples were imperfectly crystallised and held too much foreign matter of uncertain composition to make specific gravity determinations of any value.

Analyses of Calaverite.

	I. Prince Albert mine.	II. Raven mine.	III. C. O. D. mine.
Tellurium (Te)	57·27	47·69	53·89
Gold (Au)	38·95	33·93	39·31
Silver (Ag)	3·21	1·47	0·85
Insoluble	0·33	5·80	0·91
Ferric oxide (Fe_2O_3) ..	0·12 (*a*)		
Iron (Fe)		5·41	1·67
Sulphur (S)		6·17 (*b*)	1·58 (2·96 FeS_2)
Manganese (Mn) ..			0·23 (*c*)
Calcium (Ca)			0·51
Magnesium (Mg) ..			0·10
Oxygen, fluorine, and soluble silica, by difference			0·95 (*d*)
	99·88	100·47	100·00

(*a*) This was included with the insoluble matter in arriving at the corrected density.
(*b*) Calculated from the Fe to make FeS_2.
(*c*) As MnO_2?
(*d*) A part of the calcium found in solution was derived from fluorite, which likewise constituted some of the soluble matter in this instance.

Selenium has been reported to occur in traces in the district (F. C. Knight, *Proc. Colo. Sci. Soc.*, Oct. 1, 1894), but it could not be detected in the amount of mineral taken for the above analyses.

Excluding everything but gold, silver, and tellurium, and re-calculating to 100, the following comparison is obtained:—

	I.	Ratio.	II.	Ratio.	III.	Ratio.
Te ..	57·60	2·01	57·40	2·05	57·30	2·09
Au ..	39·17	1·00	40·83	1·00	41·80	1·00
Ag ..	3·23		1·77		0·90	
	100·00		100·00		100·00	

The ratio here obtaining is that for sylvanite and calaverite, but the very low percentage of silver shows that the mineral is calaverite. Indeed, the first analysis agrees almost exactly with Genth's analysis of the species. Interesting is the slight variation in the ratio between gold and silver, end the very low percentage of silver in the mineral from the C. O. D. and Raven mines. Calaverite, the lowest silver carrier of the gold-silver tellurides, has not heretofore been known to carry less than 3 per cent of silver.

The pyrognostic characterists of the mineral from the Prince Albert mine were essentially those ascribed to calaverite. In the closed tube it fuses, giving a white coating near the assay, and a globular grey coating just above, which latter by strong heat can be in part driven higher up, leaving the glass covered with the same white fused coating as lower down. This latter is yellow while hot. On charcoal the mineral fuses with a green flame, giving a white coating and similar fumes, and leaving a yellow bead. The colour is pale bronze yellow, in powder greenish grey. The hardness is not less than and perhaps a little over 3. Specific gravity, as given above, 9·00.

The identity of the telluride occurring at Cripple Creek, which in oxidising gives free gold and oxidised tellurium compounds,* seems thus satisfactorily established, but unless there is another richer in silver the mode of occurrence of the silver in some of the ores is still in large part unaccounted for. It may be derived from a very rich argentiferous tetrahedrite of which Prof. Penrose submitted a small specimen for identification. This carries over 11 per cent of silver, but is said to be excessively scarce, and therefore hardly to be considered in this connection, unless indeed this should have been the original source of most of the silver and later have suffered oxidation to a great extent, whereby the silver has become more evenly distributed throughout the ore.

Professor Penfield has kindly contributed the following notes on the crystallography of the mineral:—

"The crystals of calaverite which were examined were developed with prismatic habit, but the prismatic zone was striated to such an extent that it was impossible to identify a single face in the zone, and on the reflecting goniometer almost an unbroken band of signals was obtained in a revolution of 360°. Owing to oscillatory combinations the crystals were also much distorted, so that they did not present regular cross sections.

The prisms were attached so that doubly terminated ones were not observed, while the faces at the free end were small and developed with so little symmetry that after a study of a number of crystals it was found impossible to determine with certainty the system of crystallisation.

The crystals do not exhibit the perfect cleavage ascribed to sylvanite and krennerite, but are similar to the former in some of their angles. When placed in position to show their relation to sylvanite they have their prismatic development parallel to the *b* axis. One crystal, which owing to its development was more carefully measured than any of the others, was apparently a twin about 101, and showed at the end the forms 111 and 110. The measurements compared with the corresponding ones of sylvanite are as follows:—

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* From the *American Journal of Science*, vol. l., August, 1895.

* From tests made by myself on a number of specimens collected by Prof. Penrose the combination seems to be chiefly, if not altogether, with iron, but whether as tellurite or tellurate could not be ascertained.

			Sylvanite.	
111 ∧ (111) over twinning plane	93°	35′	94°	30′
110 ∧ (110) ,, ,,	35	2	34	43
110 ∧ 111	36	35	37	3
110 ∧ 111 in twin crystal	36	33	37	3

Other forms which were measured could not be referred to the sylvanite axes, and it seems probable from their development and lack of symmetry that the crystals are triclinic; but no satisfaction was obtained after a long and careful study of the limited supply of material on hand.

In conclusion, therefore, it may be stated that the crystals are probably triclinic, but near sylvanite in angles and axial ratio."

THE REDUCTION OF THE ACIDS OF SELENIUM BY HYDRIODIC ACID.*

By F. A. GOOCH and W. G. REYNOLDS.

A METHOD for the iodometric determination of selenious acid has been recently announced by Muthmann and Schaefer (*Berichte d. D. Chem. Gesell.*, xxvi., 1008) which is based upon the reduction of selenious acid by hydriodic acid and the direct titration of the iodine thus liberated. To determine the selenious acid it is only necessary to add it in solution to an acidulated solution of potassium iodide, when iodine and selenium are both set free in elementary form, the former being directly determinable by titration with sodium thiosulphate after addition of starch. The difficulty in the process is said to be the uncertainty as to the exact point in the titration at which the starch blue disappears from the liquid in which the finely divided and opalescent selenium is held in suspension. For this reason the process is recommended for use only when great accuracy is not essential.

Evidently if the reaction between the acidulated iodide and selenious acid is single and complete, the process should be capable of improvement by removing the selenium before the titration is attempted. This we have succeeded in doing without difficulty. We find the most convenient and rapid way to remove the finely-divided selenium is to filter the liquid containing it by means of the vacuum pump upon a thick felt of asbestos in a perforated crucible or cone of large filtering surface. With a properly prepared filter of this description there is no difficulty in separating the selenium in a very few moments so completely that it is possible to determine the iodide remaining dissolved in the excess of potassium iodide with all the accuracy characteristic of this most exact of titration processes. We find, however, that when the difficulty of determining the end-reaction in the titration of the iodine by the thiosulphate is overcome, it becomes apparent that the reaction upon which Muthmann and Schaefer depend is not perfect. Either the reduction of the selenious acid to selenium is not complete, or else the iodine remains in combination to a slight extent with the selenium and so fails to appear in the filtrate. This is evident from the results of the experiments of Table I., in which the selenious acid and potassium iodide acidulated with hydrochloric acid were brought together, the liquid thrown upon the asbestos filter, the selenium washed until free from soluble iodine, and the filtrate containing the iodine treated as usual with sodium thiosulphate in presence of starch. The details of treatment are described sufficiently in the table. The selenium dioxide was prepared for the work from the so-called pure elementary selenium by dissolving it in strong nitric acid, evaporating off the excess of the last, treating the solution of the residue in water with barium hydroxide, filtering to remove selenic acid formed in the oxidation and traces of sulphuric acid possibly present as an impurity, recovering the selenium dioxide by evaporation, and purifying it by subliming and re-subliming it in a current of dry air until it was clean and white.

TABLE I.

SeO_2 taken. Grm.	KI used. Grms.	HCl used (Sp.gr. 1 20). C.m.³	Volume before filtering. C.m.³	SeO_2 found. Grm.	Error. Grm.
0·0499	1	5	100	0·0479	0·0020 −
0·0499	1	5	100	0·0477	0·0022 −
0·2035	3	5	100	0·1896	0·0139 −

From these figures it is plain that iodine was not found in the filtrate in amount corresponding to the selenium dioxide present. In the following experiments of Table II. an excess of the thiosulphate was added before filtering off the selenium so that there should be every opportunity for the iodine and thiosulphate to interact before the removal of the selenium. In two experiments the proportion of hydrochloric acid was increased ten-fold for the purpose of seeing whether the presence of a large amount of free acid influences the result.

TABLE II.

SeO_2 taken. Grm.	KI used. Grms.	HCl used. (Sp. gr. 1·20). C m.³	Volume before filtering. C.m.³	SeO_2 found. Grm.	Error. Grm.
0·0499	1	5	100	0·0489	0·0010 −
0·0499	1	3	100	0·0485	0·0014 −
0·0499	1	50	100	0·0489	0·0010 −
0·0499	1	50	100	0·0488	0·0011 −
0·2006	3	5	100	0·1925	0·0081 −
0·2030	3	5	100	0·1945	0·0085 −

These results show improvement over those obtained when filtration is made before acting with the thiosulphate, but it is obvious that the presence of a large proportion of free hydrochloric acid is without effect upon the reaction, and that the iodine set free and measured is still deficient in proportion to the amount of selenium dioxide present. Plainly the reduction of the selenium dioxide is incomplete, or else there is formed between the selenium and iodine a combination, such as was noticed by Hautefeuille (*Comptes Rendus*, lxviii., 1554) in the interaction of iodine upon hydrogen selenide. In either case it should be possible to push the reaction farther toward completion by submitting the mixture of selenious acid, potassium iodide, and hydrochloric acid to distillation. We have used for this purpose an apparatus employed and described in connection with previous similar work in this laboratory. The distillation flask is a Voit gas-washing flask, and this is sealed to the inlet tube of a Drexel wash-bottle used as a receiver, to the outlet tube of which is sealed a Will and Varrentrapp absorption apparatus to serve as a trap. The mixture to be distilled was introduced into the flask, a solution of 3 grms. of potassium iodide in 100 c.m.³ of water was put into the receiver and trap and during the distillation a slow current of carbon dioxide was passed through the apparatus to keep the boiling regular. Naturally the acidified solution of the iodide in the flask retains with great tenacity traces of dissolved iodine, so that, in order to determine all the iodine liberated in the reaction, the residue in the flask as well as the distillate in the receiver and trap was titrated in the usual way with sodium thiosulphate. The details of treatment and the results are recorded in Table III.

These results are all fairly good, though all a little deficient, for amounts of seleninm dioxide up to 0·2 grm.; but when the amount of the dioxide reaches 0·5 grm. the iodine found in the distillate and in solution in the residue falls far below the theory based upon the assumption that the products are selenium, iodine, and water. The selenium in the residue was left after the boiling in fine dense

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* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. l., Sept., 1895.

Table III.

SeO_2 taken. Grm.	KI in flask. Grms.	HCl in flask. (Sp. gr. 1·20). C.m.³	Total volume boiled. C.m.³	Time in minutes.	SeO_2 found. Grm.	Error. Grm.
0·0499	1	5	60	5	0·0497	0·0002 –
0·0499	1	5	60	5	0·0497	0·0002 –
0·0499	1	5	60	10	0·0496	0·0003 –
0·2000	3	5	60	10	0·1995	0·0005 –
0·2000	3	5	60	10	0·1991	0·0009 –
0·2023	3	5	60	10	0·2018	0·0005 –
0·5018	3	5	60	10	0·4635	0·0383 –

crystalline condition in the experiments with the smaller amounts, so that it did not interfere with the titration of the free iodine; but in the last experiment, in which approximately 0·5 grm. of the dioxide was treated, the selenium remained in pasty form adhering to the flask. Subsequent examination proved that the pasty selenium held iodine, which was liberated slowly to water, and more rapidly to an aqueous solution of potassium iodide. The largest errors have been found (excepting that of the last experiment from the discussion) when the free iodine was filtered off from the reduced selenium; better results were obtained when the precipitated selenium was first treated with the thiosulphate before filtering; and in the distillation process the best approximations are made to true indications. It is obvious that as the proportion of selenium and iodine increase, the tendency to form a combination is more manifest. The error thus introduced in the determination of the selenium dioxide by the distillation process is allowable up to the limit of 0·2 grm.

Potassium iodide in hydrochloric acid acts much less readily upon selenic acid than upon selenious acid. When the hydrochloric acid is present in small proportions in the mixture of selenic acid and the iodide the reduction is very imperfect, but it tends to approach completion as the strength of hydrochloric acid is increased.

It is obvious, in the light of the previous experiments with selenious acid, that it is unreasonable to expect the full liberation of iodine in the action of selenic acid upon the iodine when the free iodine is not removed from the sphere of action as it is liberated. In the distillation process the case is otherwise, and there is no reason to anticipate that the determination of selenic acid should present greater difficulty than is encountered in treating selenious acid under similar circumstances. The experiments of Table IV., in which selenic acid (obtained by oxidising known amounts of selenium dioxide by means of potassium permanganate in the manner described in a previous paper from this laboratory—Gooch and Clemens, *Amer. Journ. of Science*, l. 51) is treated according to the distillation method outlined above for the determination of selenious acid, show that this expectation is realised, and that the analytical results are fairly good.

Table IV.

SeO_3 taken. Grm.	KI in flask. Grms.	HCl in flask. (Sp. gr. 1·20). C.m.³	Total volume boiled. C.m.³	Time in minutes.	SeO_3 found. Grm.	Error. Grm.
0·0593	1	5	60	5	0·0593	0·0000
0·0593	1	5	60	5	0·0591	0·0002 –
0·0593	3	5	60	10	0·0596	0·0003 +
0·1779	3	5	60	10	0·1769	0·0010 –
0·1779	3	5	60	10	0·1780	0·0001 +
0·1779	3	5	60	10	0·1764	0·0015 –

In conclusion, it is plain that while the simple contact of solutions of selenious acid or selenic acid and potassium iodide acidified with hydrochloric acid does not determine the liberation of the full amount of iodine which would be expected if selenium, iodine, and water were the sole products of action, it is possible to bring about such action with a close approximation to completeness, when the amounts of selenium present are not too large, by submitting such mixtures to distillation. We prefer, in applying the reaction to analytical purposes, to work with the apparatus and under the conditions described,—treating, preferably, not more than 0·2 grm. of the selenium oxide, using from 1 grm. to 3 grms. of potassium iodide in the distilling-flask with 5 c.m.³ of strong hydrochloric acid in a total volume of 60 c.m.³, and continuing to boil for ten minutes.

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.*

By F. W. CLARKE.

(Continued from p. 106).

Cobalt and Nickel.

The atomic weights of these two metals have been redetermined by Winkler (*Zeit. Anorg. Chem*, viii., 1), who adopts a radically new method, using the pure electrolytic elements as a starting-point. In each case the weighed metal, deposited upon platinum, is treated with a weighed excess of iodine dissolved in potassium iodide. The metals are thus converted into iodides, and the excess of iodine is then measured by titration with thiosulphate solution. Thus the direct ratios, Co : I, Ni : I, are determined. Two series of estimations are given for each metal, with results as follows. The atomic weights used in calculation are H = 1, I = 126·53.

First Series—Cobalt.

Wt. Co.	Wt. I.	At. wt. Co.
0·4999	2·128837	59·4242
0·5084	2·166750	59·3772
0·5290	2·254335	59·3828
0·6822	2·908399	59·3582
0·6715	2·861617	59·3824
	Mean ..	59·3849

Second Series—Cobalt.

Wt. Co.	Wt. I.	At. wt. Co.
0·5185	2·209694	59·3798
0·5267	2·246037	59·3430
0·5319	2·268736	59·3294
	Mean ..	59·3507

Mean of all, Co = 59·3678

First Series—Nickel.

Wt. Ni.	Wt. I.	At. wt. Ni.
0·5144	2·217494	58·6702
0·4983	2·148502	58·6918
0·5265	2·268742	58·7268
0·6889	2·970709	58·6828
0·6876	2·965918	58·6678
	Mean ..	58·6878

Second Series—Nickel.

Wt. Ni.	Wt. I.	At. wt. Ni.
0·5120	2·205627	58·7436
0·5200	2·204107	58·7732
0·5246	2·259925	58·7432
	Mean ..	58·7433

Mean of all, Ni = 58·7155.

For O = 16 these become—

Co = 59·517
Ni = 58·863.

(To be continued).

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* From the *Journal of the American Chemical Society*, vol. xvii., No. 3. Read at the Boston Meeting, Dec. 28, 1894.

WARNING AGAINST THE USE OF FLUORIFEROUS HYDROGEN PEROXIDE IN ESTIMATING TITANIUM.

By W. F. HILLEBRAND.

DUNNINGTON (*Journ. Am. Chem. Soc.*, xiii., 210) has pointed out a source of error to be guarded against in estimating titanium in rocks and minerals by Weller's method, due, as he believes, to the partial reversion, in certain cases, of ordinary titanic to meta-titanic acid, which does not afford a yellow colour with hydrogen peroxide. It remains for me to indicate another source of error in the possible presence of fluorine in the hydrogen peroxide.

For two years the colorimetric method has given reasonable satisfaction in this laboratory, but recently a new lot of hydrogen peroxide was purchased, of a different brand from that hitherto used, and, after a time, it was noticed that the results obtained were in some instances far too high, and that no two determinations agreed.

It is known that hydrogen peroxide does not produce a yellow colour in titanium solutions carrying hydrofluoric acid or fluorides, and, moreover, the addition of even a drop of the dilute acid to an already peroxidised titanium solution weakens the colour. For this reason it is necessary to take the greatest care to ensure the complete expulsion of all fluorine when dissolving rocks or minerals by means of hydrofluoric and sulphuric acids prior to the colorimetric estimation. A drop of hydrofluosilicic acid acts similarly, but the latter reagent cannot be made to completely discharge the colour even if added in great excess.

This, however, was not suspected as the cause of our trouble until, on referring to the circular of one of the leading makers of hydrogen perexide in America, whose product has always given satisfactory results in titanium work, it was found that among the various acids enumerated as usually to be found in the commercial article, hydrofluoric acid appears. Talbot and Moody, in the *Technology Quarterly*, v., 123, mention hydrofluosilicic acid as of frequent occurrence in the peroxide manufactured a few years ago. On examining the suspected peroxide by neutralising with fixed alkali, evaporating to dryness, and heating with strong sulphuric acid, fluorine was detected by the odour of the acid evolved and by its action on glass.

It is therefore imperative to use only hydrogen peroxide which is free from fluorine in estimating titanium, for its presence may utterly vitiate the results, even if only 2 or 3 c.c. of the peroxide are employed.—*Journal of the American Chemical Society*, xvii., No. 9.

DETERMINATION OF ANTIMONY AS ANTIMONIC ANTIMONIATE.

By OTTO BAUNEK.

THE method of determining antimony as antimonic antimoniate devised by Bunsen has for some time fallen into discredit, after having been formerly in almost universal use and being recommended in the last edition of the text-book of Fresenius as decidedly trustworthy. The cause is chiefly a subsequent publication of Bunsen's, in which he completely abandons as untrustworthy the method which he had previously recommended, and supersedes it by a new procedure—the determination of antimony as pentasulphide. According to his investigations the temperature of the decomposition of the tetroxide is not much higher than that of its formation, so that it is difficult to seize the point when the weight of the contents of the crucible corresponds to the tetroxide of the antimony taken. On continued ignition the weight of the crucible progressively diminishes, and even 0·1 grm. of the substance can be completely volatilised in six hours.

This observation is directly contradictory to the statements of most text-books and manuals of chemistry, even the most recent, which characterise the tetroxide as infusible and fixed on ignition. This contradiction, as well as the circumstance that the above method is still in extensive practice and has been recommended in various recent manuals of quantitative analysis, induced me to examine thoroughly the permanence of antimony tetroxide on ignition, and the consequent trustworthiness of the above method of determination.

Chemically pure antimony, obtained by reducing the purest potassium antimoniate with potassium cyanide,* was weighed off and oxidised with nitric acid, whilst the crucible was covered with a watch-glass. After the latter had been rinsed out the contents were evaporated to dryness, and the residue heated in an uncovered crucible—at first gently, and then at redness, until the weight is constant. The weight of the contents of the crucible exactly corresponded to the weight of the antimony employed as calculated from the formula Sb_2O_4. The crucible was then left uncovered for several hours at a bright red-heat without the slightest loss of weight.

In this manner an entire series of determinations was effected with different quantities of antimony. Hence it appears that, on proceeding as above, the antimonic antimoniate can be used as a form of weighing antimony.

I then sought to ascertain under what conditions antimony tetroxide may be volatilised on ignition.

A weighed quantity of antimony was oxidised in the manner above described, and ignited until the weight was constant. The lid of the crucible was then put on, and the ignition continued under otherwise similar conditions. On taking off the cover, after five minutes, its inside was found covered with shining needles of teroxide, whilst a white fume ascended from the crucible, the weight of which had naturally considerably decreased. The sintered residue was then pulverised, weighed off in a porcelain crucible of equal size, and ignited again with the same flame but without cover. After ignition for an hour not the slightest decrease of weight was perceptible. If the ignition was then repeated in the covered crucible the former phenomenon reappeared, and there was again a sublimate of teroxide on the inside of the lid.

As the tetroxide is persistent on ignition, even on the exclusion of air,—as it appears from its behaviour on ignition in a closed tube, when there appears not the slightest trace of a sublimate,—its decomposition into teroxide and oxygen on ignition in a covered crucible can be referred only to the reductive action of the flame gases—an assumption which is verified by the following experiment:—

A porcelain crucible, such as was used in the previous experiment, was suspended in a circular disk of asbestos-pasteboard in such a manner as to include tightly the edge of the crucible. The antimonic acid was then converted into tetroxide by ignition in an open crucible until the weight was constant. The cover was then put on, and the crucible heated for one hour to bright redness without any loss of weight or the appearance of a trace of sublimed teroxide. If the disk was then removed the same flame, in a very short interval, occasioned a strong reduction to teroxide.

In this manner the volatilisation of antimony tetroxide —with decomposition into teroxide and oxygen—as obtained by Bunsen is easily explained. The flame-gases are caught under the projecting edge of the cover of the crucible, displace the air in the interior of the crucible, and exert a reductive action. This is also the case if the flame does not enwrap the entire crucible, but merely

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* This reduction can be effected without fear of an explosion if a small quantity of the mixed substances is fused in a capacious porcelain crucible, and the rest is added to the glowing melt in small portions, waiting each time until the violent reaction is at an end.

its lower part. But if the interior of the crucible can freely communicate with the atmospheric air, the action of the flame-gases is suppressed.

Volatilisation may also be avoided in a covered crucible if it is very large, and if the bottom only is touched by the point of the flame. But as, on evaporating the nitric acid, some of the substance generally adheres to the sides, this method of ignition is impracticable. We have now indeed found that—

1. On igniting antimonic acid with access of air a constant weight is quickly reached.
2. The antimony oxide thus obtained corresponds to the formula Sb_2O_4.

But I have further effected some determinations of antimony as tetroxide with previous precipitation of the antimony as sulphide, the results of which demonstrate the accuracy of the method.

In order to prevent an oxidation of the precipitate along with the filter, the washed antimony sulphide was rinsed with a little water into a small capsule, and the particles still clinging to the filter are dissolved in hot ammonium sulphide, which is easily effected whilst the precipitate is moist. The solution is evaporated to dryness in a weighed porcelain crucible; the main bulk of the precipitate is also rinsed into the crucible, and again evaporated. The precipitate is then moistened with concentrated nitric acid and oxidised with fuming nitric acid, using instead of the cover a watch-glass, which is then rinsed off. The solution is then evaporated to dryness, the sulphuric acid which has been formed is cautiously driven off by heat, and the residue strongly heated in an open crucible until the weight is constant. The method is, in accuracy, at least equal to the other methods of determining antimony, and surpasses them in simplicity and promptitude of execution.

In presence of small quantities of antimony, when the inaccuracies attending weighing a precipitate along with the filter have a considerable effect upon the result, Bunsen's old method may be considered preferable to all others.—*Zeit. Anal. Chem.*, xxxiv., p. 171.

NOTICES OF BOOKS.

Poisons: Their Effects and Detection. A Manual for the Use of Analytical Chemists and Experts. With an Introductory Essay on the Growth of Modern Toxicology. By Alexander Wynter Blyth, M.R.C.S., F.I.C., F.C.S., &c., Barrister-at-Law, Public Analyst for the County of Devon, and Medical Officer of Health and Public Analyst for St. Marylebone. Third Edition, Revised and Enlarged. With Tables and Illustrations. 8vo., pp. 724. London: Charles Griffin and Co., Ltd. 1895.

We have here before us an excellent treatise, instructive and suggestive, not merely to chemical experts and students, to medical practitioners and pharmacists, but to chemical manufacturers, to legislators, and lawyers, and, if we may presume to make the suggestion, even to novelists and play-wrights and to the writers of the daily press.

The work has already passed through two editions, but it has undergone such enlargements and revisions—in accordance with the advance of science—that it may fitly be treated as a new publication.

In the "Old Poison Lore" Mr. Blyth holds that the traditions of poisons which, though producing no immediate effect, might yet prove ultimately fatal, were more than fables. Have we not a too familiar instance of this phenomenon in the bite of a rabid dog? Our author thinks that "the Asiatic poisoners were well acquainted with the infectious properties of certain malignant diseases." It might be added that they selected poisons whose effects might simulate the symptoms of natural disease.

In connection with the detection of poisoning, we may mention that it is to the Popes that science was indebted for the sanction, in the Fifteenth Century, to dissect human subjects.

The account given in the following chapter of the development of our modern methods for the detection of poisons in the body. As an epoch in toxicology is mentioned the discovery of the Marsh method of detecting arsenic, which "for the first time rendered the most tasteless and easily administered poison in the world at once the easiest of detection."

We come to that difficult question—the definition of poison. The author comments on the British law (Criminal Consolidation Act, 1861) the German statute, and the present French law. The author's own definition of poison, as given in the first edition of the present work, is—"A substance of a definite chemical composition, whether mineral or organic, may be called a poison if it is capable of being taken into any living organism and causes by its own inherent chemical nature impairment or destruction of function."

As to the classification of poisons, the author admits that no perfect classification is yet possible.

In considering the statistics of poisoning, the author holds that the higher the mental development of a nation the more likely are its homicides to be caused by subtle poison, and its suicides by chloral, morphine, or hemlock. The two leading poisons in South Britain for the decade ending 1892 are opiates and lead; carbolic acid coming third. Out of 1000 attempts in France to injure or destroy human life by poison, arsenic accounts for 331 and phosphorus for 301—two of the most painful poisons ordinarily available.

The connection between toxic action and chemical composition is discussed at some length. The researches of Dr. Blake and of Rabuteau on the comparative toxic action of metals seem to have been overlooked. The more attention has been given to the organic poisons. The author considers that the occurrence of hydroxyl appears frequently to confer poisonous properties upon the substance. In aromatic compounds the toxic power increases with the number of hydroxyls.

The substitution of a halogen for hydrogen is apt to produce narcotic substances. This section, and especially the general theory of Oscar Loew (p. 39), deserve the most careful study, experimental if possible.

The chapter on "Life Tests"—the identification of poisons by experiments on animals—has been greatly abridged, since, in consequence of the deplorable "Vivisection Act," this method of research is practically out of the reach of British chemists and physiologists. If the Society for the Advancement of Medicine by Research is still in existence, we would ask why it has never organised a laboratory, say at Calais, Boulogne, or Antwerp, where such experiments might be performed?

As regards the identification of the several poisons, the author gives some most useful precautions, and pieces of information which the expert may be suddenly called to produce. Thus, it was actually asked of a witness in the Tawell case, whether hydrocyanic acid might not have been introduced by eating apples. Now, Mr. Blyth mentions here that apple-pips contain 0·035 per cent of HCN! Attempts have in like manner been made to explain the presence of oxalic acid in the matter vomited by a patient and found in the stomach of a corpse by the hypothesis that the victim had been eating rhubarb pie or a salad containing sorrel.

A real difficulty arises in a case of nicotine poisoning if the deceased has been a heavy smoker or tobacco-chewer. How much nicotine may be introduced in this manner into a human subject it might be impossible to decide with any accuracy.

Under "Arsenic," we find a recapitulation of the salient points of the Maybrick case.

Want of space does not allow us to extend our notice of Mr. Wynter Blyth's work, but we may decidedly recommend it to every professional man who has not already familiarised himself with its contents.

Cambridge Natural Science Manuals. Physical Series. General Editor, R. T. Glazebrook, M.A., F.R.S., Assistant Director of the Cavendish Laboratory, Fellow of Trinity College, Cambridge. *Solution and Electrolysis.* By William Cecil Dampier Whetham, M.A., Fellow of Trinity College, Cambridge. Cambridge: The University Press. 1895. Pp. 296.

As a clear compact exposition of solution and electrolysis as now understood this little work will be found very valuable to students of physics and chemistry. After an account of the general properties of solution, the author goes on to describe the solutions of gases in gases, of liquids in gases, and of solids in gases.

In the third chapter the author proceeds to consider solutions in liquids, and solubility, showing the solubility of gases in liquids; the measure of solubility; Henry's law, the solutions of gases in saline solutions; the solubility of liquid and of solids in liquids; the influence of pressure and of temperature; the analogy between solution and evaporation; the solubility of mixtures, and solubilities of mixed liquids; followed by a Table of Solubilities.

In the fourth chapter we have an account of the principles of diffusion and dialysis. Mr. Whetham then proceeds to treat of the freezing-points of solutions, the determination of molecular weight, of cryohydrates, and of the melting-points of alloys.

The vapour pressures of solutions are discussed in the sixth chapter, after which, in the seventh, eighth, and ninth chapters, the author enters upon the electrical properties of solutions. Here the reader meets with an account of the ions, their migrations and velocities, the theory of dissociation, and electrical endosmose.

In the tenth chapter is shown the connection between electrical and other properties, such as chemical activity and osmotic pressure.

In the concluding chapter we find the theories of electrolysis, an interesting account of the colours of saline solutions, the general case of chemical equilibrium.

There is an appendix on freezing-points and a table of the electro-chemical properties of aqueous solutions.

The work will be found accessible to a wider circle of minds than might have been at first sight expected.

"*Sanitas.*" *How to Disinfect.* A Guide to Practical Disinfection during Cases of Infectious Illness, and in Every-day Life. London: The Sanitas Company, Limited.

This pamphlet may be considered as essentially an abridgment of Mr. Kingzett's "Nature's Hygiene"—a work which we have had much pleasure in examining. The author adduces testimonies in favour of the Sanitas preparations from the most varied authorities, from eminent physicians and surgeons down to sporting characters and dog-fanciers. He declares war against the dictum that every disinfectant, to be efficacious, must be poisonous. He contends that the "Sanitas" preparations are of the highest value, not merely in combating cholera, yellow fever, diphtheria, &c., but in destroying or banishing aphides and other scourges of our gardens or orchards, though he makes no mention of their success or failure in the treatment of the phylloxera. The Sanitas oil is recommended for banishing mosquitoes or other analogous pests. We should like to ask Mr. Kingzett whether he has ever made a comparative trial with the extract of Marsh-rosemary (*Ledum palustre*), which has done such good service against mosquitoes and sand-flies (*e.g.*, *Simulium columbaczense*) in every climate where it has been tried.

It must be remarked that the Sanitas Company, Limited, do not confine themselves to the manufacture of the preparations patented under the name of "Sanitas." They are manufacturers of, and dealers in, hydrogen peroxide, a mercuric bactericide, corrosive sublimate pellets, and sulphur fumigating candles, and even of carbolic acid, of chlorides of lime and zinc, the permanganates, and of iron and copper sulphates.

For disinfectants, indeed, the field is still large, if we may judge from the recent prevalence of epidemics.

CORRESPONDENCE.

DISINFECTANTS.

To the Editor of the Chemical News.

Sir,—The remark with which Dr. Rideal seems dissatisfied was applied to the words which he quotes in his letter. He cannot, of course, deny that sewage contains phosphates, precipitable by salts of iron, aluminium, &c. He must admit that his words, "to recover the phosphate by using the sludge as a fertiliser," were open to the construction which I placed upon them, as referring to the total phosphates in the sewage sludge of what origin soever, and he is of course well aware that valuable quantities of phosphates may be found in sludges to which neither animal charcoal nor mineral phosphates have been added. Animal charcoal is now rarely, if ever, used in the treatment of sewage.

Utterly disclaiming any intention to disparage Dr. Rideal's work, I am, &c.,

Your Reviewer.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 7, August 12, 1895.

Special Microscope for the Observation of Opaque Bodies.—Ch. Fremont.—The author, after pointing out the defects of previous devices, *e.g.*, that of Lieberkühn, describes his invention, which consists in illuminating the interior of the tube of the microscope through the object-glasses. The arrangement cannot be described intelligibly without the accompanying figure. The arrangement is said to afford a vertical illumination, very intense and perfectly defined, and to be especially adapted for microphotography.

Potassium Derivatives of Quinone and Hydroquinone.—Ch. Astre.—The author has studied the action of potassium upon quinone in ethereal or benzenic solutions and upon hydroquinone in a benzenic solution. The author, in concert with M. Ville, purposes extending his observations to other metals.

No. 8, August 19, 1895.

On Matches with Explosive Compositions. — T. Schlœsing.—The author's results impress upon us the necessity of avoiding accidental ignitions during the operations after drying. We may indeed proscribe pastes of antimony and lead, although their compounds figure in all the pastes whether ancient or of recent invention, but we cannot proscribe phosphorus, and if this body produces the fumes of its acid in the workshops we lose—at least in part—the essential advantage of the suppression of white phosphorus. Hence the substitution of explosive pastes for pastes with white phosphorus is not so simple a matter as we may be tempted to believe.

Researches on the Compounds of Mercury Cyanide with Chlorides.—Raoul Varet.—Mercury cyanide, when acting on metallic chlorides, forms compounds of the type $2HgCy_2M''Cl_2.nH_2O$. The author has made a thermochemical study of the mercury and sodium chlorocyanide, the corresponding compounds of mercury and ammonium, mercury and barium, mercury and strontium, mercury and calcium, mercury and magnesium, mercury and zinc, and mercury and cadmium.

Thermic Researches on Cyanuric Acid. — Paul Lemoult.—A thermo-chemical study, not suitable for abstraction.

Combustion-Heat of Certain β-Ketonic Ethers.—J. Guinchant.—Not suitable for abstraction,

Determination of the Heat Liberated in Alcoholic Fermentation.—A. Bouffard.—The heat liberated is between 24 and 32 cals. We must not calculate in the construction of refrigerators upon 71 cals.

On the Gum of Wines.—G. Nivière and A. Hubert.—The authors, in opposition to Pasteur and Béchamp, show that there exists a marked difference between the gum of wines and gum-arabic. The latter, when oxidised with nitric acid, only yields 35 per cent of mucic acid, whilst the gum of wine yields 70 to 75 per cent, If we boil the gum of wine with dilute sulphuric acid it yields no arabinose, but it is transformed into galactose, whilst reductive agents change it into dulcite. Gum-arabic, if heated with dilute sulphuric acid, yields arabinose, and with reductive agents it forms arabite.

No. 9, August 26, 1895.

Heat of the Solution and of the Formation of Sodium and Potassium Cyanurates.—Paul Lemoult.—The author's studies do not reveal any essential difference between the sodium and potassium salts. They show, further, that these salts are not decomposed by water.

On Apiculated Fermentation, and on the Influence of Aëration in Elliptical Fermentations at High Temperatures. — M. Rietsch and M. Henselin. — The refrigeration of musts below 30° has more decided effects than aëration. The combination of these two agencies gives the best practical results; this combination is the more indicated the more concentrated are the musts.

Utensils of Aluminium.—M. Balland.—The author's investigations have been undertaken with reference to military uses, for which the low specific gravity of aluminium is especially suitable. In the ordinary conditions of a soldier's life aluminium utensils offer a sufficient resistance to wear and friction, to the action of foods and of potable liquids. The metal takes a clouded appearance, but its weight after four months' use does not vary appreciably. Their contact with foods, &c., is of brief duration. On prolonged contact the action is more considerable. The behaviour of impure samples of aluminium—containing, as sometimes occurs, as much as 8 per cent of foreign matter—cannot be inferred from the author's experiments. Aluminium vessels should never be cleansed with soda, and solderings should be avoided as much as possible.

No. 10, September 2, 1895.

Presence of Argon and Helium in Certain Mineral Waters.—Dr. Ch. Bouchard.—(See p. 152).

Combination of Magnesium with Argon and Helium.—(See p. 153).

Researches on the Compounds of Mercury Cyanide with the Bromides.—Raoul Varet.—The author has continued his researches on the combinations of mercury cyanide with the bromides of the alkaline and alkaline-earthy metals, of zinc and cadmium. The results, thermo-chemical data, do not admit of useful abridgment. At ordinary temperatures the solutions of the bromo-cyanides, mixed with the picrate of the same bases, yield, in course of time, traces of an isopurpurate. Mercury cyanide does not act upon tincture of litmus. On the contrary, the cyanides of the alkaline and alkaline-earthy metals turn the red tincture to a blue. The solutions of the bromo-cyanides, contrary to the chloro-cyanides, turn litmus slightly blue even in the cold.

Formation of Hydrogen Selenide.—H. Péladon.—This paper requires the accompanying diagram.

Action of Carbonic Acid, of Water, and of Alkalis upon Cyanuric Acid and its Dissolved Sodium and Potassium Salts. — Paul Lemoult. — This paper, essentially thermo-chemical, does not admit of useful abstraction,

The Eclipsoscope, an Apparatus for observing the Chromosphere and the Solar Protuberances.—Ch. v. Zenger. — The description of this instrument should be accompanied by diagrams.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 113.

Report presented by M. Jordan on behalf of the Committee of the Chemical Arts on F. Osmond's Paper entitled "A General Method for the Micrographic Analysis of Carbon Steels."—The method in question was in the first place due to Dr. H. C. Sorby, of Sheffield, who in 1864 laid before the British Association micro-photographs of various sorts of steel and iron, and elaborated a process for the study of the sections of the metals as preferable to fractures. Prof. Maters, of Berlin, in 1878, seems to have independently taken up the same line of research. MM. Osmund and Werth, of Creusot, further developed microscopic metallography. The former, in a paper here inserted, summarises the results hitherto obtained, and gives an account of the procedure to be adopted. In polishing the sections the author was induced to make use of liquorice-water in conjunction with jewellers' rouge and precipitated calcium sulphate, and found that it coloured certain constituents, leaving others untouched. After the polishing the action is continued by means of acids, halogens, principally nitric acid and tincture of iodine. The characteristics of iron and steels, with their peculiar constituents, ferrite, martensite, troostite, cementite, and sorbite, are shown in an illustration.

Report presented by M. Jordan on behalf of the Committee of Chemical Arts on the Researches of Mr. Hadfield on the Alloys of Iron with Silicon, Aluminium, and Chrome.—Mr. Hadfield's researches on chrome-steels are pointed out as of exceptional practical importance.

No. 114.

Elimination of Foreign Metals during the Production of "Best Selected" Copper.—Allan Gibb.—From the *Institute of Mechanical Engineers.*

Preparation and Properties of Pure Melted Molybdenum. — Henri Moissan. — The substance of this paper has already been noticed in connection with the *Comptes Rendus.*

No. 115.

The meeting of June 28th, 1895, was taken up with a notice of the prizes awarded for various inventions. Very few of these interest the chemist. F. Osmond obtained a prize of 2000 francs for a study of the physical properties of alloys in common use, especially steels. Jules Garcon obtained a prize of 500 francs for an account of the machinery employed in bleaching and dyeing textile fibres. The prize for the purification of potable waters, amounting to 2500 francs, has been divided among four candidates—MM. Tellier, Lacroix, Schlumberger, and Meignen. Tellier proposes to sterilise water by the combined action of heat and pressure. Lacroix decomposes water by the electric current, liberating hydrogen, and generating ozone and "electrolytic oxygen." Schlumberger passes the water over pumice saturated with aluminium benzoate, and then over charcoal coated with manganese peroxide; this double filtration is said to destroy the greater part of the organic matter and almost all the bacteria. The process of Meignen is not described.

Communication by C. Bardy on the Process for Treating Crude Turpentines.—Gabriel Col.—The advantages of this process depend entirely on the structure of the plant employed.

The Determination of Small Quantities of Arsenic.—Ad. Carnot.—Noticed under the *Comptes Rendus*.

Reduction of Silica by Coke.—H. Moissan.—Also noticed under *Comptes Rendus*.

MISCELLANEOUS.

Special Manures.—Messrs. W. H. and L. Collingridge have just published a book on "Special Manures for Garden Crops," by Dr. A. B. Griffiths, F.R.S.E., F.C.S. The work contains about eighty analyses of plant-ashes (which represent over eighteen hundred separate weighings), performed by the author and his pupils. The work is quite unique and original.

Serpent Venoms. — According to Professor T. D. Fraser (*Transactions of the Royal Society of Edinburgh*), the venom of the cobra is sixteen times more powerful than that of the rattle-snake (*Crotalus horridus*). The "diamantine snake" of South Australia—a species not sufficiently identified—is intensely virulent, as of its venom 0·0015 grm. is equivalent to 0·004 grm. of rattle-snake poison.

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THE CHEMICAL NEWS.

Vol. LXXII., No. 1871.

THE
ACTION OF NITRIC ACID ON CERTAIN SALTS.*

By H. A. AUDEN, B.Sc., and G. J. FOWLER, M.Sc.

The experiments here recorded are part of a systematic investigation into the conditions of stability of the oxides of nitrogen. They are by no means complete, but the results so far obtained appear to be of sufficient interest to warrant a preliminary notice.

The reactions of nitric oxide have so far alone been studied. The gas was prepared by Emrich's method, viz., the interaction of sodium nitrite, strong sulphuric acid, and mercury. The mixture was kept in continual agitation by a specially contrived stirrer worked by a turbine. In this way a regular stream of gas is obtained, which analysis showed to be of a high degree of purity.

In order to study the action of nitric oxide upon the salts selected, a weighed amount of the salt was placed in a boat contained in a Lothar Meyer constant temperature furnace. By means of a thermostat, also devised by Lothar Meyer, the temperature can be kept to within one degree. Temperatures above the range of an ordinary instrument were measured by means of a high temperature thermometer, constructed by Max Kaehler and Martini, of Berlin, which would give accurate readings to over 400°. The salt was heated gradually in a stream of nitric oxide and the phenomena noted as the temperature rose; the salt was weighed at different intervals of temperature, so that it was possible to tell at what temperature reaction began, and at what point it attained a maximum velocity.

So far, oxy-salts have been chiefly studied. It was thought that by comparing their behaviour under the above conditions some light might be thrown on their stability and thence on their constitution. One or two oxides were fixed examined, the results agreeing with those of Sabatier and Senderens, *e.g.*, PbO_2 forms a basic nitrate of lead when heated in nitric oxide; the action begins at a temperature as low as 15°, but does not attain its maximum till over 130°.

MnO_2 behaves similarly, but the change is not so rapid as in the case of PbO_2, probably owing to the smaller stability of manganese nitrate. The change is most rapid at 216°. In neither case with a peroxide are any but traces of a nitrite formed.

Silver oxide, however, at any rate if at all moist, yields a mixture of almost equivalent parts of silver nitrite and metallic silver at the ordinary temperature. At higher temperatures, with the dry oxide, nitrate and metallic silver are formed almost entirely.

Silver permanganate begins to be attacked at the ordinary temperature, and at 80° the alteration is very rapid. On analysis of the residue it was found to consist of metallic silver, silver oxide, silver nitrate, and manganese dioxide. Very little, if any, manganese nitrate was formed.

Potassium permanganate is much more stable than the silver salt. It is not appreciably attacked till over 100°, and the increase in weight becomes rapid at 190°. The residue on moistening was not alkaline, and no manganese could be dissolved out. The potassium is converted into nitrate and the manganese into oxide.

Interesting differences were noted in the behaviour of other silver and potassium salts, notably the chlorates and iodates.

Potassium chlorate is attacked by nitric oxide at the ordinary temperature, chlorine being evolved in considerable quantity, and nitric peroxide being formed. The gaseous product was condensed in a tube immersed in a freezing mixture, and the percentage of chlorine in the brown liquid obtained was determined. It was found to be much in defect of that required to form nitrosyl or nitroxyl chloride, so that the reaction does not consist simply in the formation of an oxy-chloride of nitrogen. On analysis of the residue in the boat no chloride of potassium was found to be present. Nitrate was formed, and also a slight trace of perchlorate. This seems to be direct proof that in potassium chlorate the potassium and chlorine are separate.

With barium chlorate a similar reaction took place.

With silver chlorate (prepared according to Stas's method), chlorine was given off, but a considerable amount of silver chloride was also formed—nearly one-third of the silver present being found as chloride. This may be due to a difference in constitution between the chlorates of silver and of potassium, or to a difference in stability of the products of reaction. That some difference of constitution exists between the silver and potassium salts appears to derive confirmation from the behaviour of their iodates when treated with nitric oxide.

Potassium iodate, heated to 80° in nitric oxide, begins to give off iodine, and the reaction becomes rapid at 110°, crystals of iodine condensing on the cool portion of the tube. No trace of iodide, however, is formed, as is shown by there being no liberation of iodine on acidifying a solution of the residue after adding some potassium iodate. The residue is not alkaline, the potassium being converted into nitrate, recognised by the evolution of ammonia when the residue is warmed with zinc-dust and caustic soda.

Silver iodate, on the other hand, is stable up to a rather higher temperature than the potassium salt, and when heated above this temperature, about 110°, no trace of iodine is given off, but all the silver is converted into iodide, none being dissolved out by water, and the yellow residue being insoluble in dilute nitric acid.

The perchlorates and periodates which have been examined show themselves more stable than the corresponding chlorates and iodates.

Potassium perchlorate does not begin to be attacked till above 200°. A small quantity of chloride was found in the residue, but the high temperature (over 300°) employed may have induced secondary changes. The potassium for the most part is converted into nitrate, there being considerable loss of chlorine.

Barium periodate is stable up to 200°, when iodine is given off. On heating to 388° much iodine is given off, and barium iodide found in the residue.

Of the salts so far examined, chromates have shown themselves the most stable, being analogous in this respect to the sulphates.

Lead chromate was unaltered at a temperature exceeding 400°.

Silver chromate did not suffer appreciable change till above 300°. Metallic silver was found to be present in the residue as well as silver nitrate. The chromium was all converted into the sesquioxide. Some amount of nitrite of silver was also formed. Silver sulphate is only slightly attacked at the highest temperature of the furnace.

It was found in certain cases, *e.g.*, with lead nitrate, that the intermixture of a decomposable oxide, *e.g.*, PbO_2 or MnO_2 with the salt caused the latter to be attacked at a temperature below that at which action begins with either the salt or oxide taken separately.

Experiments have also been in progress on the interaction of nitric oxide and various gases, but the results are not yet quite complete enough for publication.

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* Read before the British Association (Section B), Ipswich Meeting, 1895.

THE FORMATION AND PROPERTIES OF A NEW ORGANIC ACID.*

By HENRY J. HORSTMAN FENTON, M.A

When tartaric acid is oxidised under certain conditions in presence of a ferrous salt a substance is produced which acts as a powerful reducing agent, and which gives a beautiful violet colour with ferric salts in presence of alkali. This substance has after considerable difficulty been isolated, and proves to be a dibasic acid having the formula $C_4H_4O_6.2H_2O$.

The constitution of this acid is now under investigation.

Heated with hydrogen iodide it gives succinic acid, racemic acid being an intermediate product. Bromine in presence of water oxidises it quantitatively to dioxytartaric acid. Heated with water it is resolved into carbon dioxide and glycollic aldehyd.

This aldehyd has been obtained as a viscid liquid, pure except for a trace of ether; and, on removing the latter by heating in a vacuum, the aldehyd undergoes polymerisation, a sweet-tasting solid gum being the result. Analysis and molecular weight determinations show that this gummy substance has the formula $C_6H_{12}O_6$ (*Journ. Chem. Soc.*, 1894, 899; 1895, 48 and 774).

Further observations have recently been made as to the conditions under which this new acid may be obtained from tartaric acid. The presence of a *ferrous* salt is essential. Ferric, manganous, and various other salts have been tried with negative results.

If moist ferrous tartrate be exposed to the air for a short time a certain quantity of the new acid is produced, and may be indicated by the characteristic violet colour given when caustic alkali is added. The effect is much more intense if the exposure be made out of doors, and the increased result was at first attributed to some constituent of the fresh air (*e.g.*, hydrogen dioxide; ozone seems to be inoperative). But later experiments show conclusively that *light* is the cause. Air which has been purified by passing through potassium iodide and caustic potash solutions gives an effect about equal in intensity to that produced by fresh external air, if the exposure to light is the same in both cases. That *oxygen* (or some oxidising agent) is essential is shown by the fact that exposure in a vacuum, even to bright sunlight, gives a negative result.

DATA FOR THE ASCERTAINMENT OF THE TRUE ATOMIC WEIGHT OF CARBON.

By J. ALFRED WANKLYN.

In December, 1893, I wrote in the *Philosophical Magazine*:—

"An investigation which has occupied me for the greater part of the year has yielded the following result. There is a series of hydrocarbons the successive members of which rise in molecular weight—not by $CH_2=14$—but by $\frac{1}{2}(CH_2)=7$. If this result cannot be overturned, the consequence follows that the atomic weight of carbon is 6."

The series concerning which I wrote at the close of the year 1893 was the hydrocarbons existing in Russian kerosene imported into this country. That series would, according to the prevailing knowledge of the day, be termed a series which was only imperfectly understood. Continuing our work, my colleague Cooper and myself have recently published (*Philosophical Magazine*, August, 1895) a parallel investigation with a parallel result, given by a series of hydrocarbons which the knowledge of the day pronounces to be comparatively well explored and well understood. The series is the marsh gas series, which is now regarded as the backbone of organic chemistry.

The paper published last month in the *Philosophical Magazine* contains a concise statement of our work, and we proceed to quote from it as follows:— . . .

The first term of the marsh gas series which figures in our table is the fifteenth member of that series. In an admirable paper of Schorlemmer's, published in the *Journal of the Chemical Society* for the year 1863, a liquid is described under the name of hydride of heptyl, which we believe contained at least 50 per cent of our marsh xv. (formula $C_{15}H_{17}$). Quoting from that paper we find that a combustion of the liquid gave 83·93 per cent of carbon, 16·13 per cent of hydrogen, and the determination of vapour density 3·59, which is a figure between that required for hydride of heptyl and our marsh xv., and which indeed approaches nearer to that required by marsh xv. than to the figures required by hydride of heptyl.

The figures are theoretical V.D. of marsh xv. = 3·697; theoretical V.D. of heptyl hydride 3·455. Obviously therefore the figures obtained by Schorlemmer, 3·59, agrees better with our view than with that held by himself thirty years ago.

As I hold that the only datum given in Schorlemmer's paper which is valid as a piece of evidence capable of deciding between the two formulæ is the V.D. determination, I hope I may be pardoned for going over Schorlemmer's calculation, the correctness of which I am able to confirm. I make, however, this note, there is no mention made of the size of the inevitable air-bubble in the Dumas-determination, and if we suppose that this air-bubble was of the usual size when the workmanship is excellent (as Schorlemmer's workmanship always was), the correction for the air-bubble would bring Schorlemmer's figures very close to marsh xv.

A consideration of all the circumstances of the case leads me indeed to the belief that Schorlemmer's hydride of heptyl of the year 1863 consisted mainly of marsh xv., mixed with hydride of heptyl.

The main body of Schorlemmer's paper, which I am at present quoting, is occupied with an account of the chlorination of the hydrocarbon and the various derivatives of one of the products of the chlorination. It is an admirable piece of chemical workmanship, and deserves proper appreciation.

There are two classes of reaction in organic chemistry, viz., the complete and the incomplete.

Chlorination of such a body as marsh xv., or heptyl hydride, is notoriously an incomplete reaction. This fact becomes very apparent in Schorlemmer's account of the operation. It is impossible to take a quantity of the hydrocarbon and transform the whole of it, or anything like the whole of it, into a monochloride. Only a portion of the hydrocarbon undergoes chlorination in this operation and the "unattacked hydride," as Schorlemmer says, was distilled off after the termination of the chlorination. The monochloride was then separated by fractional distillation from the accompanying di-chloride, and from the still more highly chlorinated products which are the inevitable companions of the mono-chloride as yielded by the process of chlorinating a hydrocarbon. The mono-chloride (which is described as a liquid boiling at 150°) does not appear to have been submitted to analysis, but was employed in the preparation of the acetic ether by reaction upon acetate of potash. Great difficulty was experienced in pushing the reaction to completeness, and, furthermore, *only a portion* of the mono-chloride underwent transformation into the acetic ether. The olefine heptylene as well as acetate of heptyl are described by Schorlemmer as arising from the reaction upon acetate of potash.

The acetate of heptyl described by Schorlemmer was therefore derived from the original hydrocarbon by two incomplete reactions, and is not a fair representative of

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* Read before the British Association (Section B), Ipswich Meeting, 1895.

the whole of the original hydrocarbon. The acetate was analysed and its analysis agreed with the formula for acetate of heptyl. It was also converted into the corresponding alcohol by a process which is known to be complete when applied to the acetate. The alcohol was also converted in a thoroughly satisfactory manner into the iodide, and both alcohol and iodide were analysed with good results, the iodide especially being beautifully in agreement with the theory. When these results are fairly considered they indicate the probability that some portion of the original hydrocarbon consisted of heptyl-hydride, but they afford no ground for the conclusion that the whole or even the greater proportion of it consisted of that hydride. There is a curious piece of evidence pointing in the other direction. The olefine (which accompanies the acetate of heptyl) was investigated. It was sealed up with hydriodic acid and heated to the boiling point of water for twelve hours and converted into an iodine compound, which on analysis was found to contain only 55·73 per cent of iodine instead of 56·19 required by the iodide of the heptyl series.

The circumstance that the other iodide gave almost exactly the theoretical result, viz., 56·18 per cent of iodine, lends importance to this discrepancy, which Schorlemmer does not in any way explain.

A by no means unlikely explanation of the discrepancy is that the iodine compound was a mixture of the derivative from our marsh xv. with the derivative from hexyl-hydride.

In criticising this work of Schorlemmer's nothing is further from my intention than to belittle it. A very important general fact is established by it and by the researches of Cahours and Pelouze and Carius. That fact is, that one atom of hydrogen in the marsh gas series of hydrocarbons is replaceable by chlorine, which in its turn suffers replacement by other radicals so as to yield the alcohol, the mercaptan and the various ethers. Until, however, the chlorination process has been much improved it cannot be valid as a method of distinguishing between heptyl-hydride and the fifteenth term of the marsh gas series.

In due time we expect to exhibit the intermediate alcohols and their various derivatives, but at present we have no intention of taking in hand this branch of the investigation. We are at present engaged with the physical side of the subject, and with only such chemical changes as do not involve the destruction of the hydrocarbons.

Inasmuch as the process by which we have been able to separate the hydrocarbons from one another is fractional distillation, we have applied ourselves to the task of measuring the vapour-tension of the individual hydrocarbons at different temperatures.

Every chemist knows that the every day operation of taking the boiling point of a liquid is in point of fact a special vapour-tension observation, and that the boiling point is another name for that point of temperature at which the tension of the vapour of the liquid is equal to 760 m.m. of mercury, the average pressure of the atmosphere. Instead, therefore, of using a distillatory apparatus and observing the temperature registered by the thermometer immersed in the vapour of the liquid during distillation, we might arrive at the same result by the employment of the apparatus for measuring the tension of the vapours evolved by liquids at different temperatures.

The apparatus which we employ we have ourselves constructed, and one of its peculiar advantages is that by its aid we are able to ascertain the boiling point of a very minute quantity of liquid. A single decigramme of a specimen of liquid is amply sufficient for such determinations.

Our work in this direction is only just at the commencement, and this map of vapour tensions is a preliminary chart (a chart accompanies the paper), exhibiting part of the curve of tension of eleven consecutive terms of the kerose series.

The *Tensio-meter* (as we name our new instrument) has a future rich in promises. In carrying out the fractionation of a mixture of liquids boiling very near together, it provides a criterion indicative of the completion of the fractionating process. When the distillation has been pushed to complete dryness there will always be a few drops of residual liquid on allowing the retort to cool. When the tension of those few drops approximates to the tension of the original liquid—that is a sign that the fractionation has reached completeness, and the Tensio-meter enables that comparison to be made.

Light on the question whether, in a given instance, there is specific adhesion between the constituents of a mixture may be looked for by having recourse to this instrument, which imparts a degree of certainty and completeness to the fundamental operation of fractional distillation which has hitherto been altogether wanting.

In conclusion I exhibit four terms of the marsh gas series, viz.:—

Marsh xi.	formula	$C_{11}H_{13}$
Marsh xv.	,,	$C_{15}H_{17}$
Marsh xvi.	,,	$C_{16}H_{18}$
Marsh xvii.	,,	$C_{17}H_{19}$

In presence of these substances chemists will be compelled to revert to that atomic weight of carbon which was all but universally admitted forty years ago.

Laboratory, New Malden, Surrey.

ON THE FORMATION OF CITRIC ACID BY THE OXIDATION OF CANE-SUGAR.

By EDWIN F. HICKS.

Some time ago Dr. Phipson, in the Chemical News (vol. lxxi., p. 296) announced that he had obtained an acid which he regarded as citric acid, as a result of the oxidation in the cold of an acidulated (H_2SO_4) solution of cane-sugar with permanganic acid. After the solution became clear, it was carefully neutralised with ammonia, calcium chloride solution was added, and the solution on boiling gave the precipitate which was described as containing citric acid.

Soon after this announcement, Messrs. Searle and Tankard repeated Dr. Phipson's work with great care (Chemical News, lxxii., 31), and although they obtained a precipitate on neutralising, adding calcium chloride and boiling, it did not in any way resemble calcium citrate. On the contrary, this precipitate was proved, by analysis and microscopical examination, to consist in every case of hydrated calcium sulphate, $CaSO_4.2H_2O$. Further, when nitric acid was used for the acidulation in place of sulphuric, no precipitate was obtained on treating and boiling the solution as before.

Previously to the work of Searle and Tankard I had done some few experiments according to the directions given in Phipson's note. Owing to lack of time my results obtained then were not conclusive as to the nature of the precipitate, except that I could not confirm it as being calcium citrate according to any of the ordinary tests for citric acid.

Recently, having more time at my disposal, I again undertook to repeat the experiments, following out the directions given by Dr. Phipson as exactly as possible, but varying the conditions in order to note any difference in the course of the reaction with different relative amounts of acid and permanganate, as well as the concentration of the solution. My results in every way corroborate those anticipated by me in the work of Searle and Tankard.

The results of my experiments may be briefly summarised. When the solution contains a greater quantity of H_2SO_4 than 1 to 100, precipitation takes place on standing in the cold; and for equal concentration and permanganate added, is greater the more acid present. On filtering and boiling further precipitation takes place.

When the amount of acid present is less than 1 to 100, no precipitation takes place in the cold, but on boiling a finely crystalline white precipitate is formed, its relative amount bearing the same relation to the amount of acid present as in the first case. On adding alcohol to the filtrates from these precipitates a further precipitate is thrown down. All the precipitates obtained were thoroughly washed with boiling water.

One description will suffice for all, whether obtained by precipitation in the cold, after boiling, or on treating the filtrates with alcohol. In every case they consisted entirely of pure hydrated calcium sulphate, $CaSO_4.2H_2O$. No trace of any organic acid was found. All the precipitates were finely crystallised and easily identified with the microscope, which was supplemented by obtaining the confirmative chemical tests.

I also used a nitric acid solution and obtained results identical with those described by Searle and Tankard (*loc. cit.*).

In conclusion, it would seem that this work, although largely a repetition, is not altogether out of place, as Dr. Phipson in a second note (Chemical News, vol. lxxii., 100), not having repeated his experiments, seems to doubt the conclusions, and has pointed out certain possible errors of conditions in the work of the two chemists mentioned above.

I think my work has completely covered these conditions, and can leave no doubt as to the composition of the precipitate, and has further shown that it is obviously futile to look for the formation of citric acid, unless other conditions than those specified are admitted.

52, Beaver Street, New York City.
September 16, 1895.

ON THE
VOLUMETRIC DETERMINATION OF METALS.
By H. LESCŒUR.

L. Barthe has recently given a process for determining the free acid and the metal in a salt of zinc containing acid in excess. To this end he uses a normal alkali and two indicators, phenolphthalein and the colouring matter of the red hollyhock. He ascribes to the precipitate formed by the alkaline solution in the salt of zinc at the moment when the phenolphthalein turns of a rose colour the composition of a basic salt, $(ZnO)_4SO_4Zn$. Hence it is necessary to multiply the number of c.c. of the normal solution of potassa by $\frac{5}{4}$ in order to calculate the metal in the manner usual in volumetry.

For several years I have employed for the volumetric determination of metals in salts in presence of an excess of acid a method almost identical with that of Barthe. As an indicator I use simultaneously methyl-orange (Orange No. III. of Poirrier) and phenolphthalein. The former indicating by its gooseberry tint the presence of a free acid, and becoming decolourised by the addition of alkali at the exact moment when neutrality is reached; the second indicating the moment when free potassa exists in the mixture, and showing by its change the end of the precipitation. As for zinc, I have not observed the formation of a sub-salt. Analysis shows that the product collected at the moment of the change of colour of the phenolphthalein, after washing and desiccation, is zinc oxide. Perhaps the washings effected after precipitation have destroyed the basic salt?

The following experiment shows that this is not the case, and destroys the hypothesis of Barthe:—

One grm. of commercial zinc sulphate, titrated with normal soda (caustic), required 6 c.c. of the solution to turn the colour of the phenolphthalein (a result corresponding only to 0·861 grm. of $ZnSO_4.7H_2O$). The precipitate is collected upon a filter, washed with boiling water, and re-dissolved in hydrochloric acid. But on the one hand, the *washings do not contain zinc*, and on the other hand, *the hydrochloric solution does not contain sulphuric acid.*

The precipitate is therefore zinc oxide free from sulphate. The method is only rendered more simple, no correction being necessary, and the normal solutions of soda and zinc being volumetrically equivalent.—*Bull. de la Soc. Chim. de Paris.*

ON THE DETERMINATION OF BORIC ACID.
By H. JAY and M. DUPASQUIER.

Among all the procedures for determining boric acid, that with methylic acid is the most trustworthy, as it enables us to isolate with accuracy the total product to be determined. The modification which we have introduced into this method, which consists in the manner of distillation, and the peculiarity of the titration, enables us to apply it in all cases, which was not practicable with the operation as hitherto described.

The substance in question, dried and pulverised, after being freed from any organic matter, is acidulated with hydrochloric or sulphuric acid in very small excess, introduced, along with 25 to 30 c.c. of methylic alcohol, into a flask fitted with a cork having two perforations. One of these orifices admits a perpendicular tube bent at its lower end, descending almost to the bottom of the flask and traversing a refrigeratory at its upper part. The other orifice admits a delivery-tube leading into a second flask, like the former, and plunging to the bottom. A second delivery-tube, sealed to the perpendicular tube, enters the second flask, which before the commencement of the operation receives 1, 2, or 3 c.c. of a normal solution of potassa or soda (freed from carbonic acid), according to the supposed quantity of boric acid, and having always an excess of alkali.

The two flasks, when connected, are heated separately in the water-bath. The methylic alcohol conveys the boric acid from the first flask to the second, in which it is retained by the alkalis, finding its way into the refrigerator to re-descend again, effecting in a continuous manner the complete extraction even of large proportions of the boric acid. The time consumed by the operation is variable, but for 300 m.grms. it does not exceed ninety minutes.

After having experimented with various indicators, we prefer litmus paper and the blue C. L. B., the latter already indicated by Engel.

The alkaline liquid containing the boric acid is gently heated so as to expel the methylic alcohol and to be concentrated to a constant volume; it is then rendered slightly acid by means of a few drops of dilute hydrochloric acid, warmed afresh to volatilise any traces of carbonic acid which have been introduced during the distillation. We cool to 15—20°, and titrate with a decinormal solution of potassa or soda free from carbonic acid until a small drop placed upon litmus paper is found neutral. Then follows the titration of the boric acid. We add to the liquid two drops of an aqueous solution of blue C.L.B., at 10 grms. per litre, and pour anew the titrated liquid until the first change of tint. The quantity of liquid employed, after deducting 0·2 c.c. or 0·3 c.c., according to volume, indicates exactly the proportion of boric acid present.

The conditions necessary for obtaining exact results are uniform volumes and constant temperatures, as also the elimination of the carbonic acid and of methylic alcohol.

In a series of experiments on wines to which known quantities of boric acid had been added along with, in some cases, hydrochloric acid and fluorine compounds, the authors found that hydrofluoric acid alone effected a slight excess of the proportion introduced, and falsified the results to that extent. But they believe that this slight excess may be neglected in practice. The process has been further verified upon wines of different growths, upon ciders, perries, and wines.—*Comptes Rendus*, cxxi., p. 260.

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.*

By F. W. CLARKE.

(Continued from p. 157).

Palladium.

In 1889 Keiser published his determinations of the atomic weight of palladium, for which, since then, other investigators have found somewhat different values. He has now, jointly with Mary B. Breed, given a new set of determinations, which confirm his former series (*Am. Chem. J.*, xvi., 20). As before, palladiammonium chloride was reduced in hydrogen, the salt being prepared by two methods and carefully examined as to purity. Two series of experiments are given, with the following weights of material:—

First Series.

$Pd(NH_3Cl)_2$.	Pd.	At. wt. Pd.
1·60842	0·80997	106·271
2·08295	1·04920	106·325
2·02440	1·01975	106 334
2·54810	1·28360	106·342
1·75505	0·88410	106·341
	From sum of weights ..	106·325
	Reduced to vacuum ..	106·246

Second Series.

$Pd(NH_3Cl)_2$.	Pd.	At. wt. Pd.
1·50275	0·75685	106·297
1·23672	0·62286	106·296
1·34470	0·67739	106·343
1·49059	0·75095	106·353
	From sum of weights ..	106·322
	Reduced to vacuum ..	106·245

The atomic weight was computed with H = 1, N = 14·01, and Cl = 35·37. If O = 16 this becomes Pd = 106·51. This is only 0·02 less than the value obtained in the earlier investigation.

Tungsten.

A new determination of the atomic weight of tungsten, by Pennington and Smith (read before the American Philosophical Society, Nov. 2, 1894), leads to a much higher value than that commonly accepted. The older work seems very probably to have been done upon material contaminated with molybdenum, an impurity which was eliminated in this investigation by Debray's method,—that is, by volatilisation by means of gaseous hydrochloric acid. The metal, carefully purified, was oxidised in porcelain crucibles, with all necessary precautions, and the following data are given:—

Wt. W.	Wt. O_3.	At. wt. W.
0·862871	0·223952	184·942
0·650700	0·168900	184·923
0·597654	0·155143	184909
0·666820	0·173103	184·902
0·428228	0·111168	184·900
0·671920	0·174406	184·925
0·590220	0·153193	184·933
0·568654	0·147588	184·943
1·080973	0·280600	184·913
	Mean ..	184·921

All weights are reduced to a vacuum, and O = 16 is taken as the standard of reference.

Another paper, by Smith and Desi, was read at the same meeting with that just cited. In this research, the tungstic oxide was purified in the same way, and reduced by heating in a stream of pure hydrogen. The water formed was weighed, and all weights reduced to a vacuum. Computed with O = 16 and H = 1·008, the results are as follows:—

Wt. WO_3.	Wt. H_2O.	At. wt. W.
0·983024	0·22834	184·683
0·998424	0·23189	184·709
1·008074	0·23409	184·749
0·911974	0·21184	184·678
0·997974	0·23179	184·704
1·007024	0·23389	184·706
	Mean ..	184·704

Why this result should be lower than that previously found by Pennington and Smith remains to be explained.

(To be continued).

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

Introductory.

The investigation of the elastic forces or tensions of vapours emitted by a solution of a fixed substance in a volatile liquid has received much attention, especially within recent years. The impetus for investigations of this kind is, in a great measure, due to the new notions that have been introduced into science in regard to the nature of solutions. The possibility of ascertaining the molecular mass of a substance from a determination of the amount of the depression of the vapour-tension of a liquid, occasioned by its being dissolved therein in known proportions, has induced chemists to study carefully this field of scientific inquiry, which it may truly be said has been gone over very elaborately.

In the greater part of the work that has been done, both theoretical and experimental, it has been assumed that the dissolved substance is not appreciably present in the gaseous state, and but sparingly present in the liquid state; in other words, the dissolved substance is supposed to be involatile, and the solutions are made dilute.

Now, absolute involatility in any body whatsoever cannot be affirmed; there must always be, at every temperature, some degree of power of assuming the gaseous state, although it may be so slight as to be imperceptible to our senses. Still, for all practical purposes, the assumption of non-volatility in many substances can be admitted, as our means of experimentation are not sufficiently delicate to detect any small amount of volatility.

Although so much has been done on the vapour-tensions of solutions of fixed substances in volatile liquids, comparatively little attention has been paid to the study of the vapour-tensions of mixtures of the volatile liquids; yet this is the general case, of which the restriction that the dissolved substance be fixed makes only a special application. It must, indeed, be allowed that the consideration of a mixture of vapours, instead of a single one, introduces certain complications into the problem; and this is, perhaps, just the reason so little work has been done on this part of the subject; still difficulties of this sort are probably not unsurmountable.

The limitations of work on vapour-tensions to dilute or, at most, moderately concentrated solutions cannot be

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* From the *Journal of the American Chemical Society*, vol. xvii., No. 3. Read at the Boston Meeting, Dec. 28, 1894.

* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

said to be satisfactory. True, the theory of solutions has been developed on the hypotheses that dissolved matter, in analogy with gaseous matter, is in a state of considerable dilution; and experimental confirmations of theoretical predictions can be expected only when such a state of affairs is realised. Nothwithstanding that circumstance, it seems of importance to extend our line of operations and attack the problems presented by concentrated solutions; perhaps they will be found to exhibit fewer anomalies than has been supposed.

There are two circumstances which render work that has hitherto been done on the vapour tensions of mixtures of volatile liquids of all concentrations unsatisfactory; they are to be found in the choice of the liquids investigated, and the kinds of vapour-tension measured. The liquids chosen were almost invariably those which are now recognised to be made up of associated molecules; they are just those which exhibit the greatest abnormalities in respect to most of their properties, and it cannot be expected that simple relations, if they exist at all, will be discovered when such liquids are used as material of investigation. All investigators also, almost without exception, have measured only the total pressure of the mixtures of liquids examined, which is the sum of the partial pressures, these, however, being entirely unknown. But more important is it to know the share which each vapour has in the exerting of the total pressure, and only when this is learned can our knowledge of the matter be said to be in any adequate measure complete.

This paper seeks to fill in some degree this gap in the subject of vapour-tensions. The method employed is such as to permit of the specification of the partial pressures of a mixture's components, and also of their concentrations in the gaseous phase. The choice of the liquids has been made with an eye towards employing those which have been found to be most "normal," so that in the examination of more complex liquids, that is, those consisting of associated molecules, the simplicity to be expected in the phenomena of the former may aid us in getting some light on the possible intricacies of the latter. All the mixtures examined are freely soluble in one another, so that no disturbing influence from layer-formation can take place.

In reality, we have before us a case of equilibrium; the equilibrating system consists of two substances, each present in two phases, the liquid and gaseous. We have to ascertain at the points of equilibrium the temperature, the partial pressures of the two substances in gaseous phase, and their concentration in both liquid and gaseous phase.

Description of Apparatus.

It is of prime importance in the determination of vapour-tensions that the temperature be kept uniform; accordingly I describe, first of all, the apparatus employed for that purpose.

Thermostat.—This consisted of a cylindrical copper vessel holding nearly forty litres of water. It was heated by means of a ring burner; the pressure of the gas was kept constant by means of a pressure-regulator, and a thermo-regulator as described by Ostwald (*Ztschr. Phys. Chem.*, ii., 565, 1888), controlled by combustion of the gas. To insure uniformity of temperature in all parts of the bath, the water was kept in constant agitation by means of a number of fine streams of air blown up through it, the laboratory being provided with air under pressure. Such a means of agitation gives very satisfactory results; it takes up but very little room, and permits of the examination of the pieces of apparatus plunged in the water by shutting off for a few seconds the flow of the air.

The temperature of the bath remained constant to within 0·05° during an experiment; the thermometer employed was one graduated to tenths of degrees, and had recently been tested by the "Physikalische Reichsanstalt" of Berlin.

The apparatus consisted of three principal parts, each made up from material easily found in almost every chemical laboratory. The first part consists of those pieces required to measure a definite volume of air, to compress it enough to force it through the apparatus, and to dry it thoroughly; the second part is the contrivance for saturating the volume of air with the vapour of the liquid under examination; and the third is the arrangement for the analysis of the gaseous mixture.

First Principal Part of Apparatus.—This consists of a measuring vessel, a vessel for regulating the internal pressure, a manometer, and a system of drying tubes. I pass to the description of each.

The Measuring Vessel consists of an ordinary bottle of a capacity varying from one to three litres, according as it is required to employ a larger or a smaller volume of air; the height of the bottle should be such that only the neck is above the water; in its neck is fitted a good rubber stopper through which passes one branch of a T tube. This branch of the T tube is made of tubing of about a quarter inch bore, and is about eight inches long, while the other branch has only half this bore, with a length of about 3 inches. The wider branch of the tube is pushed through the stopper so that its lower edge is just flush with that of the rubber, and care is taken that this adjustment is in every experiment maintained, as well as that the stopper is always inserted to the same distance in the neck of the measuring vessel. In the upper end of the wider branch of the T tube is inserted (an air-tight joint being assured by the use of rubber tubing) a tube somewhat drawn out and narrowed at its lower end, and provided with a stop-cock at its upper end. The end of the lower part must be about a half inch above level of the stop of the measuring vessel, and the upper end is put, by means of a piece of rubber tubing, in communication with a water supply at constant level about a yard above the thermostat. If the stop-cock be opened water will flow into the vessel, and displace the air therein contained which escapes through the side branch, which, being in the middle of the vertical branch, is an inch or so above the orifice of the tube introducing the water.

Sufficient mercury is poured into the vessel to make it sit firmly on the floor of the thermostat. The residual volume of the vessel is carefully determined by pouring into it from graduated vessels, enough water to fill it up to the level with the upper surface of the stopper. If the adjustment of the stopper and the tubes be always the same, duplicate determinations of the capacity do not differ by more than one-half c.c. If the same volume of mercury always be taken, the volume of water will represent the volume of air passed through a liquid or mixture of liquids undergoing investigation in all determinations.

It is superfluous to make corrections for the expansion of the mercury and the glass when determinations of vapour-tensions are made at higher temperatures, as the error of the estimation of the capacity exceeds the amount of the corrections.

The Pressure Regulator consists of a bottle of any convenient size, provided with enough mercury to make it stand steadily under water, and fitted with a twice perforated rubber stopper. Through one of the holes of the stopper passes a tube nearly to the level of the mercury and furnished with a stopcock at its upper end; this tube is connected by means of rubber tubing with the same water source as the measuring vessel. In the other hole is fitted a T-tube, of which one of the horizontal branches is connected by means of a bit of stout rubber with the narrower branch of the T-tube belonging to the measuring vessel, while the other is attached by rubber tubing to the other parts of the apparatus. If water be run into the bottle serving as pressure regulator, the air in it is compressed until it can force itself through the liquid with the vapour of which it is to be saturated.

The Manometer is intended to measure the amount of this compression or the internal pressure; it is made of ordinary glass tubing bent into U-shape, with the branches about two feet long. It may be put between the measuring vessel and the pressure regulator, or between the drying tubes and the latter; I have found it most convenient, however, to melt it into the vertical branch of the T-tube of the measuring vessel just opposite the horizontal branch, as shown in Fig. 1. The manometric liquid is water, and the differences of the heights of the liquid columns of the two branches, is read to a millimetre by means of a metric rule; the readings are then easily exact to a tenth m.m. of mercury.

The Drying Tubes can, of course, be of various shapes and filled with various drying agents. Liquids, such as strong sulphuric acid, must be rejected, however, as they increase the internal pressure, and often cause an irregularity in the flow of the gas. I found U-tubes to be the best shape, and grains of pumice stone, soaked in concentrated sulphuric acid, the best drying agent; a length of at least 60 c.m. is to be taken, and the pumice must be changed often. When it becomes necessary, in work on acid solutions, to remove the carbon dioxide from the air, an additional tube filled with soda-lime is taken. At the end of the last U tube, a mercury valve is attached to prevent the backward diffusion of the vapours; this is of the smallest size convenient, and the delivery-tube dipping into the mercury of capillary dimensions.

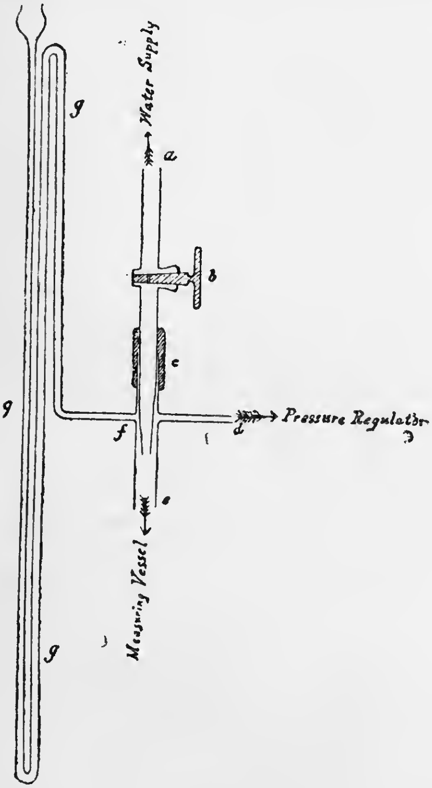

FIG. 1.

Second Principal Part of Apparatus.—This is the absorption vessel. which may consist of a simple potash bulb according to Mohr. I found it better, however, to add two more bulbs, making five small and two large ones. As liquids which dissolve rubber somewhat were often introduced into the apparatus, and as it was necessary to let it stand some time before weighing, the outlet and inlet tubes were provided with tiny ground glass stoppers. At first the bulbs were shut up in a copper case set in the thermostat; the case had holes in its sides, below the surface of the water, for the conduction and abduction of air, platinum capillaries and ground glass caps being employed to make the connections. This arrangement was not, however, found satisfactory, since one was never sure, air being such a bad conductor of heat, that the contents of the bulbs had the same temperature as that of the bath. Also, the platinum tubes proved to be very delicate, breaking readily if bent often, which was inevitable. It was accordingly found best to plunge the absorption vessel directly into the water of the bath, connection with the system of drying tubes being made with a bit of stout rubber tubing of small bore. When the vessel was removed from the water it was carefully wiped dry and set in the balance case, the atmosphere of which was kept dry by means of concentrated sulphuric acid.

Third Principal Part of Apparatus.—In order to analyse the mixture of vapour issuing from the absorption vessel two modifications of this part of the apparatus are required—one to be employed when the gaseous mixture contains a halogen compound of carbon, and the other when it contains an acid. In the first, the compound was decomposed by heated lime, and, in the second, the acid was absorbed by a solution of potash or baryta. In the following lines a description of each is given.

1. The outlet tube of the absorption apparatus is fitted by means of a good cork into one branch of a U-tube of rather thick glass; this branch is bent at right angles at about the middle of its length, while the other branch is left straight. The latter branch is held clamped to a heavy, and hence steady, retort-stand set beside the thermostat, and is connected by means of a narrow lead tube to a tube of hard glass placed in the gutter of a combustion furnace. In the further end of the hard glass tube, a Maquenne absorption apparatus, containing a little dilute nitric acid, is inserted, the connection being made with a rubber stopper; this outlet of the absorption apparatus is in communication with a suction pump, and in the rubber tube making this connection a T-tube is interposed, over the open end of which is slipped a piece of rubber tubing long enough to reach to the thermostat. When this tube is open, the interior of the apparatus, up to the liquid in the absorption vessel, is under atmospheric pressure; if it be pinched together a little so as to prevent enough air to feed the suction pump from entering, the pressure in the apparatus may be made less than that of the atmosphere; by this little device it is possible to regulate the pressure with great nicety.

2. This analysing apparatus consists simply of a potash bulb, according to Liebig, made of thick glass; one branch is flared out to receive the outlet tube of the absorption vessel, and the other is straight so as to glide up and down in a clamp of a retort-stand.

The pieces of apparatus just mentioned will receive complementary description in the directions for performing experiments.

Performance of an Experiment when the Mixture contains an Organic Halogen or Sulphur Compound.—The hard glass tube (about 80 c.m. long) is filled with lime or sodium carbonate just as in a determination of halogens in organic analysis, joined to the lead tubing which establishes communication with the U-tubes held in a clamp just above the surface of the water in the thermostat, and placed in the furnace. The gas is now lighted and the tube with its contents heated up to a red heat, while a current of dried air is passed through it to remove all moisture.

The measuring vessel, the pressure regulator, and the system of drying tubes are joined air-tight together, and so set in the thermostat that as much room as possible is left for the absorption vessel.

The absorption vessel is filled with the liquid or solution under examination, a few bubbles of air drawn through so as to get the liquid beforehand in the right position, and carefully weighed. It is then connected with the U-tube (of course, no air is now being passed through the analysing tube), and after a couple of minutes of half-submersion in the bath, it is attached to the system of drying-tubes. It is now wholly submerged in the bath and air is made to pass through it as follows:—

The stopcock of the pressure-bottle is opened so that water may be run in slowly and, by compression of the air, gradually increase the internal pressure. As soon as bubbles of air commence to pass out of the absorption vessel, the stopcock of the pressure-regulator is closed, and that of the measuring vessel opened. The water issues in drops or a fine stream in full sight of the operator, and its rapidity of flow can be very easily regulated. Experience has taught me that about a litre an hour was about the best rate; after a brief acquaintance with the apparatus, it is possible to judge very closely from the rate of the flow how long it will take for the measuring vessel to become filled. While the operation is proceeding, the height of the manometric column is read off at several different times; if the rate of flow is constant this does not vary by more than 1 or 2 m.m. of water, or less than one-tenth m.m. of mercury.

The barometer is also read off at the beginning and at the end of the experiment; in all my determinations, the difference of the two readings was less than one m.m. of mercury.

A minute or so before the measuring vessel is full, the absorption-bulbs are lifted out of the water enough to bring the end-tubes about 2 inches above the surface, and there, together with the joining tube on one side and the cork and end of U-tube on the other, are carefully dried with filter-paper. When the water in the measuring flask has reached the mark on the T-tube (level of cork), the absorption vessel is detached from the drying-tubes, and the little glass stopper fitted into its inlet tube. Immediately after this operation the connection between the absorption vessel and the U-tube is broken, and as soon as this is done a perforated cork, through which passes a narrow glass tube so bent at right angles that a long vertical branch is obtained, is fitted into the U-tube, its object being to prevent the escape by diffusion of any portion of vapour contained in the U-tube. A current of air is now drawn through the tubes, slow at first to avoid causing too much vapour to pass over upon the heated lime all at once, as, if there be a deficit of air, the combustion is incomplete, and free carbon collects in the cooler portion of the tubes; in a well-conducted experiment, the lime should remain perfectly white. Towards the end of the determination, a more rapid stream of air is drawn through the apparatus, so that one may be sure that all the halogen compound has been brought into contact in the decomposing agent. If any free carbon collects in the tube, or if the dilute nitric acid in the Maquenne absorption-bulb shows on the addition of silver nitrate the slightest trace of cloudiness, the determination ought to be rejected as untrustworthy.

The absorption vessel, as soon as possible after its removal from the water in the thermostat, should be closed with the second tiny stopper, wiped dry, and set in the balance case, where it takes on the temperature of the room. When this is thought to have taken place, it is weighed, and the loss of weight set down as the evaporated quantity of solution. When the furnace has cooled down the lime tube is removed, and its contents washed out with water and nitric acid into a flask, which is set over a flame and boiled until complete solution ensues, more nitric acid being added if necessary. If more than a half grm. of the halogen compound has evaporated, the solution is brought to a certain volume and an aliquot portion of it taken for analysis.

Most of the analyses were made by the gravimetric method of determination of halogens by precipitation with silver nitrate; some, also, were analysed volumetrically, Volhard's method being employed.

Performance of an Experiment when the Mixture contains an Acid.—The absorption vessel is filled with the mixture being investigated, and weighed as described above. It is then joined by means of a good cork to the analysing apparatus, into which are run from a pipette 10 c.c. of a stock solution of potash or baryta; the pipette being provided with a straight calcium chloride tube filled with soda-lime, all contamination from the carbonic acid of the breath is avoided. The alkaline liquor is of such strength that it is more than sufficient to neutralise the vapourised acid. The further end of the analysing arrangement is closed with a U-tube filled with soda-lime, so that the alkaline solution may be in contact with an atmosphere free from carbon dioxide.

The two pieces of apparatus thus filled and joined together are submerged in the water of the thermostat, the whole being held in place with a clamp embracing the upright tube of the analysing contrivance and attached to a heavy retort stand. The other end of the absorption vessel is then placed in communication with the drying tubes, &c., by means of a short bit of stout rubber tubing.

The internal pressure is regulated and the air passed just as described in the preceding section, note being taken of the amount of internal pressure, the volume of the air, and the barometric height. A slight correction has to be made to the barometric reading for the following reason:—After the air passes the liquid contained in the absorption vessel, and comes into the analysing tube, it is under a pressure equal to that of the atmosphere plus that due to the weight of a column of liquid corresponding to the difference of level between the two surfaces of the alkaline solution; this, in my apparatus, was determined to be equal to 1 m.m. of mercury, which was added to all barometric readings.

When the measured volume of air has passed through the apparatus, the stopcock, through which water enters into the measuring vessel, is closed, the absorption and analysing vessels are lifted nearly out of water, and after the joint between the absorption vessel and the system of drying tubes has been wiped dry, it is broken. Both the pieces of apparatus are wiped dry with bibulous paper, and agitated somewhat so that any acid vapours in the bulbs may be brought in contact with and absorbed by the alkaline liquor.

The pieces are then disconnected, the absorption vessel stoppered and set in the balance-case, while the contents of the analysing vessel are poured into a beaker, rinsing being done with water free from carbon dioxide. Without delay, the excess of alkali is estimated by titration against decinormal acid solution, and by a simple calculation the quantity of evaporated acid is obtained.

(To be continued).

OBITUARY.

THE LATE LOUIS PASTEUR.

On September 29th Science, and especially the science of France, underwent a severe loss in the person of Louis Pasteur, one of the most successful students of that world of wonders, "the infinitely little." In our brief notice of the illustrious deceased we must first point out that he was not a medical practitioner, not even in the strict sense of the word a biologist. He was essentially a chemist—of course, in the French and German acceptation of the term. His earliest scientific studies and his first discoveries were on chemical questions. His scientific education was developed at the Ecole Normale, an institution which permits and even encourages individual effort. He observed for the first time the characteristic difference between tartaric and paratartaric acid, the crystals of the former having no plane of symmetry in common with those of the latter. He separated the double sodium and ammonium paratartrate into two salts having an inverse action on the plane of polarisation of light. The welcome which this capital discovery received from Biot and other leading Academicians won for Pasteur the position of Assistant Professor of Chemistry at the University of Strasburg. His researches now led him to the conclusion that all the products of inorganic nature are not dissymmetrical. while vegetable and animal products are atomically dissymmetrical. In this characteristic he hoped to find the key to the problem of animating inorganic matter. He discovered a connection between the researches of chemistry and crystallographic physics, and the dawning results of physiological chemistry. His attention was now turned to the study of fermentation. He was nominated Dean of the Faculty of Sciences at Lille. As the district is largely interested in the manufacture of alcohol, he resolved to devote a course of lectures to the study of fermentation. He soon recognised the influence of the presence of a living organism. This view involved him in a controversy with Liebig, which ultimately terminated in the recognition of the new theory which was found applicable in the manufacture of vinegar. Liebig, it must be added, declined Pasteur's challenge to submit the question to an experimental investigation before an Academic Commission.

Next arose the question of spontaneous generation. Redi, Spallanzani, and Swammerdam denied the possibility of this alleged process. Aristotle, Buffon, and Pouchet affirmed it. It became the duty of Pasteur to take a decisive part in the contest. He had just been entrusted with the scientific studies at the Ecole Normale. But he had no laboratory, and had to furnish one at his own expense in a garret at the Ecole Normale! At last Pouchet and Joly, his opponents, withdrew from the contest. It must be remembered that the cause of spontaneous generation—heterogeny—suffered severely from the experiments of Tyndall.

The importance of Pasteur's researches has since been extending. They have thrown a new light on the manufacture of wine and beer, and on the propagation of disease, both in man and in the lower animals. At the present time we are on the point of recognising in a development of Pasteur's researches, a means of conferring on man immunity against malaria and against the bites of the most deadly serpents.

Surely we may pronounce the life-work of Louis Pasteur glorious, alike from the point of view of pure science, and that of practical utility; glorious to himself and to his country.

NOTICES OF BOOKS.

Die Genesis der Elemente von William Crookes. Ein Vortrag gehalten in der " Royal Institution " zu London, am 18ten Februar, 1887. (" The Genesis of the Elements, by William Crookes: a Discourse delivered at the Royal Institution of London, on February 18th, 1887.") Brunswick: Friedrich Vieweg and Son. 1895.

We have before us the second edition of the German version of Mr. Crookes's Discourse on the " Genesis of the Elements."

The translation is from the pen of Prof. Dr. W. Preyer, who is not merely a thorough English scholar, but whose researches have been to a considerable extent devoted to kindred subjects. Hence he has been able and willing to present to the German scientific public the views of Mr. Crookes not only *accurately* but *fairly*.

This double qualification is no mere tautology. Just as an orator can lead his hearers astray without ever being guilty of technical falsehood, so a writer in transferring profound scientific speculations into a foreign tongue may discredit them without laying himself open to the charge of inaccuracy. The author, without accepting the views of Mr. Crookes as a creed outside of which there is no salvation, admits that the picture which he has drawn of the development of the chemical elements is worthy of the highest attention. He considers that " whatever objection the physicist may take, there is, from a purely chemical point of view, in the chain of thought neither a chasm nor a sin against recognised facts." He tells us, in his Preface, that " there is probably no single living chemist who, *e. g.*, assumes that *e. g.* cerium and lanthanum have always existed in the quantity now present." It appears to him quite inadmissible that each of the several elements of the earth's crust must have existed at all times in exactly the present quantities. " Hence elementary mutations of matter must have occurred, or must still occur, in regions of the universe other than the small cold crust of our earth, mutations by which new elements have arisen and may arise from simpler materials."

We cannot, however, help pointing out that both Mr. Crookes in his original discourse (p. 2, line 3) and Prof. Preyer seem to assume—the former overtly and the latter by implication—that Prof. Mendeleeff recognises the evolutionary origin of the elements.

Prof. Preyer contends further, in his Preface, that even if the entire cosmogonic hypothesis of condensation, rendered probable by Kant and Laplace, is superseded by something preferable, the discourse of Mr. Crookes has—for the present at least—a special value, on account of his peculiar method of utilising the method of fractional precipitation and of spectral synthesis.

Prof. Preyer's preface will be valuable to German students as showing his exact position in reference to the views of Mr. Crookes, and to elemental evolution in general.

We find here, also, a series of appendices of great interest. In the first of these, concerning elements and meta-elements (see a Discourse delivered by Mr. Crookes at the Annual Meeting of the Chemical Society, March 28th, 1888), Prof. Preyer writes:—" A fact hitherto overlooked is in a remarkable connection with the hypothesis of Prout, resting as it does on a purely evolutionary foundation. The atomic weights of hydrogen and the seven elements of the first stage of condensation (hence the eldest and those of the simplest structure) come nearest to whole numbers (Li, G, Bo, C, N, O, F). In the elements of the second stage only four display this approximation; in those of the third stage only three; and in those of the fifth only two. Hence in the simpler elder elements the meta-elements play a quite subordinate part, but become more prominent in those formed subsequently, as the hypothesis of Crookes would demand."

A second appendix discusses the identical spectra of different substances. The identity of the spectra obtained by Crookes on a prolonged fractionated precipitation of the yttrium derivatives reminds him of the spectral identity of the hæmoglobines colouring the blood of all red-blooded animals. Prof. Preyer has found the absorption spectra of the red blood-pigment of certain insect larvæ (*Chironomus*), of a mollusk (*Cardita sulcata*), and the common earthworm (*Lumbricus*), are identical with the red blood-crystals of vertebrate animals. Notwithstanding this universal agreement in a fundamental property, the hæmoglobines differ from each other physically and chemically. Their solubility, crystallisability, and their proportion of crystalline water differ. They crystallise in at least two systems. Their quantitative composition, their coagulability, their liability to decompose, differ according to the species. If species have been modified in the course of long eras, the hæmoglobines—though fulfilling all the conditions of a true chemical compound—must have become modified step by step with the species (in a morphological sense). Hence we see that the conception of evolution must necessarily find a place in chemistry, not merely as regards the elements, but as regards the formation of highly complicated though crystalline compounds.

The scheme of the pedigree of the elements is expounded and illustrated in a third appendix.

A fourth appendix relates to Radiant Matter and the

Phosphoroscope, as displayed by Mr. Crookes at the Meeting of the British Association held at Sheffield, on August 22nd, 1879.

The Organic Elements form the subject of a fifth appendix. Hence Prof. Preyer raises the question why only the organic elements, H, C, N, O, F, Na, Mg, Si, P, S, Cl, K, Ca, and Fe, in the living vegetal and animal tissue, can keep up the vital process. He refers to the treatise "On Chemism in Living Protoplasm," by himself and Wendt (See *Himmel und Erde* for October 1st, 1891; Berlin, Hermann Pretel).

The last appendix treats of Argon and Helium. Prof. Preyer thinks the assumption that argon is a modification of nitrogen not more improbable than that of its discoverers, who regard it as a totally new element. But he holds that there are no such objections to the elementary character of helium. In conclusion, he remarks that the main difference between our present systematic chemistry, on the one hand, and our present systematic natural history on the other, in comparison with the former chemistry and natural history, is that we were formerly content with artificial, *i. e.*, arbitrary systems, whilst in our present systems we have to regard not merely that which now exists, but that from which it has been evolved. Such systems are not arbitrary, but natural, since they follow the course of Nature: they are genetic.

Polytechnic Institute of Brooklyn. The Course in Practical Chemistry.

This prospectus gives an account of the equipment and organisation of the Brooklyn Polytechnic. Foremost stands a body called the "Corporation"— equivalent, we presume, to the Senatus Academicus in German seats of learning. Next comes the "Faculty," in which chemistry is not too copiously represented. There is only one Professor of the science, the widely-known Dr. P. T. Austen. The two "Instructors" in quantitative and qualitative analysis, and the assistants in chemistry, take apparently a lower rank. Some departments seem, on the contrary, to be over-represented. Thus we find a professorship of history and philosophy, a principal of the academic department, a professorship of ancient languages, a professorship of physical science and engineering, besides another of applied mathematics and engineering, and one of physics and electrical engineering. Doubts may arise as to the respective boundaries of these departments.

In the studies of the Chemical Course we find some— as it seems to us—superfluous matter, such as logic, moral philosophy, rhetoric, debates, perspective. We fear that such an introduction of extraneous matter will infringe upon the time and the brain-power needed for Science. We are glad to see that, in the laboratory work of the Chemical Course, spectrum analysis is not omitted. Nothing is said about microscopy and microbiology.

There is an illustration showing a corner of the library, the chemical lecture-room, the laboratory for qualitative analysis, in which the students have their faces all turned in one direction, and of the laboratory for qualitative analysis.

We have full confidence in the efficiency of Prof. Austen as the head of a chemical college, but we fear his hands will not be quite free.

Programme of the Royal Technical High School at Aix-la-Chapelle for the Year of Studies 1895—1896. ("Program der Königlichen Technischen Hochschule zu Aachen.") Opening October 1st and ending July 31st, 1896. Aix-la-Chapelle: C. H. Georgi.

This eminent Polytechnic School continues to prosper. The number of students for 1894—1895 was 259 as against 236 in the previous year. The divisions are— I. Architecture; II. Constructive Engineering; III. Mechanical Engineering; IV. Mining and Metallurgy, Chemistry, and Electro-chemistry; V. General Sciences, especially Mathematics and Natural Sciences.

In Faculty IV. the professorial staff includes Dr. Andreas Arzruni (mineralogy and petrography), Dr. Ludwig Claisen (organic chemistry), Dr. Classen (inorganic chemistry and electro-chemistry), F. Dürre (metallurgy and assaying), Dr. Holzapfel (palæontology and geology), and Dr. Stalschmidt (technical chemistry). In addition there are two *docents* and ten assistants.

In Faculty VI. we find that H. Storp gives instruction in industrial hygiene, Dr. W. Müller in first assistance in sudden accidents, and Anton Lieven, M.D., gives a course of practical bacteriology.

The school has a mineralogical institute, comprising a museum and laboratory; a laboratory for analytical and inorganic chemistry, including electro-chemistry; a laboratory for organic chemistry; a museum of chemical preparations; a laboratory for technical chemistry; a physical museum and laboratory; and a botanical institute.

The full course of study in each faculty extends over four years. The lectures and the practical work in botany are compulsory only for "food-chemists."

During the autumn recess (August and September) there take place excursions to mines, metallurgical and chemical work, conducted by professors of the departments concerned. No expert can examine this prospectus without being impressed with the complete and thorough-going character of the courses of instruction given at Aachen. It may even be questioned whether the courses of study prescribed are not in some cases so comprehensive as to sin against the principle of the division of labour.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 11, September 9, 1895.

Nitro-Substitutions.—C. Matignon and M. Deligny. —The authors give a comparative table of the combustion-heats with those of the substances in which substitution is effected, and they propose the law that the isomers of position have the same combustion-heat, excepting errors of experiment. It is therefore sufficient in these thermic studies to operate upon a single one only of the three terms, the ortho, meta, or para. The differences oscillate around 4·5 cal., and are sensibly constant.

Explosion of Endothermic Gases.—L. Maquenne.— Not suitable for useful abstraction.

No. 12, September 16, 1895.

Researches on the Phosphates of Algeria. Case of a Phosphatic Rock of Bougie presenting the Composition of a Superphosphate.—H. and A. Malbot.— The authors have made a comparative study of several phosphates from the Department of Constantine, some of which are remarkable for their richness in phosphoric acid, such as thosk of Bordj-bou-Arreridg, and others for their friability, which renders them fit for immediate utilisation as plant food. The phosphatic rock of Bougie is extremely interesting, as containing phosphoric acid in three different conditions. The white portion contains 13·29 per cent of phosphoric anhydride soluble in water, 8·51 per cent insoluble in water but soluble in ammonium citrate, and 11·70 per cent insoluble in water and in ammonium citrate; in all 33·50 per cent of phosphoric anhydride. The red portion of the rock contains 2·03 per cent of phosphoric anhydride soluble in water, and 12·39 per cent soluble in ammonium citrate. The white or exterior portion, after desiccation in the stove, loses 21·42 per cent at dull redness. Unless this is done, there is an error in deficiency if the phosphoric acid is determined by precipitation as magnesium-ammonium phosphate in a citric solution, as compared with the result obtained by precipitation as ammonium phosphomolybdate. After ignition at a red heat the two methods agree absolutely.

Bulletin de la Société Chimique de Paris.

Series 3, Vols. xiii.-xiv., No. 8, 1895.

Crystalline Compound of Ferrous Chloride with Nitric Oxide.—V. Thomas.

Ammoniacal Salts of Silver.—A. Reychler.—The author gives a table showing the results of his cryoscopic experiments on these salts, proving that the addition of 2 mols. ammonia per equiv. of silver or copper scarcely at all modifies the molecular lowering of the congelation-point. He adds theoretical considerations on the constitution of the ammoniacal silver salts.

Action of Formic Aldehyd upon the Amines and on their Salts.—R. Cambier and A. Brochet.

Hexachlorobenzene Parabichloride.—Et. Barral.—The decomposition of carbon chloride, C_6Cl_8, by heat or by the majority of reagents into hexachlorobenzene and chlorine, $C_6Cl_8 = C_6Cl_6 + Cl_2$, shows that it is an addition product of hexachlorobenzene, in which the position of the two Cl is given by (1) its transformation into tetrachloroquinone under the influence of oxidising agents; (2) its preparation by means of tetrachloroquinone and phosphorus pentachloride.

Constitution of α-Hexachlorophenol and of Quinone.—Et. Barral.—The author shows that the formula of Fittig gives the constitution of quinone, and that it is a diketone, possibly of a peculiar kind.

Basic Properties of the Rosanilines and their Sulphonic Derivatives. A Reply to M. Prudhomme.—A. Rosenstiehl.—The author explains the formulæ which he has assigned to acid magenta and to sulphonic rosaniline. He shows what he has said in his former publications of the basic functions of the rosanilines, and he lastly examines whether the magentas should be regarded as ethers or as salts.

Are the Magentas Ethers or Salts?—A. Rosenstiehl.—There exists in the derivatives of triphenylmethane an assemblage of compounds in which the alcoholic function varies in a continuous manner between two extremes, as in the mineral oxides the acid function and the basic function vary, though it is not easy to draw a boundary. To unite the formulæ of an ether and to call it a salt is to collide against a word.

Analysis of the Gastric Juice.—J. Winter.

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. xxx., No. 3.

Rapid Determination of Phosphorus in Steels.—The most practical procedure consists in transforming the phosphorus into phosphoric acid, precipitating it with molybdic reagent, and determining the apparent volume of the precipitate after having effected its rapid settlement and its regular heaping up by means of centrifugal force. This method, proposed by Eggertz in 1860, was not at first appreciated as it deserved, but since 1887 it has been studied and improved, and is now in regular use. Various authors describe methods of operating slightly different. Von Jüptner proceeds as follows:—He weighs out, for medium proportions, 2 grms. of the sample (more for low percentages, and less for highly phosphidic steels), dissolves in 30 c.c. of nitric acid (sp. gr. 1·2), completes the oxidation by means of permanganate, and then causes the manganic precipitate to disappear by means of a small quantity of oxalic acid. To the solution is added 0·75 grm. of ammonium nitrate, the mixture is heated to 60°, and treated with 50 c.c. of the molybdic solution. The temperature is kept at 60° until the precipitation is completed, and then left to settle until the liquid is perfectly clear. The liquid is decanted, and the precipitate is washed into a special vessel by means of a washing-bottle charged with ammonium nitrate. The receiving vessel is contracted at its lower part and terminates in a narrow tube graduated in cubic millimetres in which the precipitate is collected. The graduated vessels, thus charged, are introduced into a small turbine, which is set in motion at the rate of 1000 rotations per minute, a speed which is kept up for four minutes. After stopping the rotation, the volume of the precipitate is read off on the graduated tube. If the surface of the precipitate is not perpendicular to the axis of the graduated tube, we read the level of the lower part and that of the upper part and take the mean. To find the proportion of phosphoric acid in the steel assayed from the volume of the precipitate, Ledebur gives the figure of 0·0025 per cent per cubic millimetre, when operating on 0·882 grm. of steel, which is equivalent to 0·0022 per cent if we operate upon 1 grm., or 0·0011 for 2 grms.

Zeitschrift fur Analytische Chemie.

Vol. xxxiv., Part 3, 1895.

Contributions to the Analysis of Must and of Wine.—A. Halenke and W. Moslinger.—This paper is too voluminous for insertion.

Contributions to the Isolation, Quantitative Separation, and Chemical Diagnosis of Alkaloids and Glykosidous Substances in Forensic Cases, with especial reference to their Detection in Putrescent Human Bodies.—Dr. Kippenberger.—This memoir also does not admit of abstraction.

New Process for the Determination of Indigotin.—Josef Schneider (*Casopis pro Prümysl Chemicky*, 1893).

Remarks on the Sweet Wines of Austria-Hungary.—Leonhard Roesler.—A memoir not calculated to interest our readers. We mention merely the fact that more than half of the samples of Tokay and analogous wines contain per litre more than 0·55 grm. of phosphoric acid.

Determination of Sulphur and Chlorine by means of Sodium Peroxide.—A. Edinger.

New Method of Separating Copper and Cadmium in Qualitative Analysis.—Allerton S. Cushman.—Already inserted.

Analysis of the Nitrogenous Components occurring in Meat Extracts and in Commercial Peptones.—A. Stutzer.

Detection and Determination of Metals in Fatty Oils.—H. Fresenius and A. Schattenfroh.

MISCELLANEOUS.

City and Guilds of London Institute.—At the recent Matriculation Examination of the City and Guilds Central Technical College, 76 candidates presented themselves, and 62 have been admitted to the College. The highest place was taken by M. Solomon, to whom the Clothworkers' Scholarship of £60 a year and free education has been awarded.

Spontaneous Combustion of Wool.—It is not sufficiently known that wool, if packed in bales whilst in a damp state, is, like cotton, liable to what is called spontaneous combustion. The action is not as violent in wool as in the case of vegetable fibre, and it has never yet been known to spread to other kinds of goods in the same ship or warehouse. But wool sometimes arrives in England scorched, and seriously deteriorated in value.

Steam-Boiler Explosions.—During the year 1894 no fewer than 35 such calamities occurred in Germany. The number of the sufferers was 34, of whom 12 were killed, 9 severely wounded, and 13 slightly injured. The most frequent causes are said to have been insufficient supply of water and local weakness of the plates from age.—*Chemiker Zeitung.*

New Poisons.—The Cape *Agricultural Journal* is calling attention to a poison not yet fully understood. It is obtained from *Acocanthera venenata* (or *Toxicophlœa Thunbergii*), known to the colonists as Gift-boom or Poison-tree. The leaves have proved rapidly destructive to many goats, and a decoction of the bark of the root is used medicinally by the native quacks, sometimes with fatal effect. In one case, where the medicine was administered as an enema, death ensued in about two minutes. It is conjectured that the active principle is not an alkaloid, but a glucoside. No analysis of the poison has been published, nor have its reactions been studied. The arrow-poison used by the Bushmen is said to be prepared by mixing the venom of the African cobra with the gum-resin which exudes from the rhizomatous base of the "gift-boll," *Brunsvigia toxicaria.* Whether the latter ingredient has any effect beyond preventing the cobra poison from being rubbed off the point of the arrow has yet to be ascertained.

Max Dreverhoft's Filter-papers.—We have received from Max Dreverhoff, of Dresden, a price-list and a number of samples of excellent filter-papers. No pains appear to have been spared to produce papers to meet the requirements of all departments of chemistry. M. Dreverhoff has succeeded very well in the great aim of all manufacturers of filters, to produce a paper that will allow liquids to pass rapidly and at the same time retain very fine precipitates. We notice the special filters that have been treated with HCl and HF: these appear to be quite strong, and a 9 c.m. circular paper on incineration leaves only 0·00006 grm. of ash. Filters of this quality, at the very reasonable prices at which they are offered, will prove a great boon to the chemist. We also note the ready-folded filters as being neatly made, and not unreasonable in price. M. Dreverhoff's price-list is very complete, giving minute particulars of all his manufactures, and, for the greater convenience of foreign customers, some of the more important announcements are given also in French and English; but in this latter endeavour the writer has unfortunately got a little mixed—for after various slips in the body of the list, he gravely expresses a belief that "the filters must satisfy the highest pretensions of the most painful analytical chemist." We trust they will prove of better quality than the English.

A New Safety Paraffin Lamp.—We are glad to find that manufacturers are becoming alive to the dangers that accompany the majority of cheap paraffin lamps, and, taking warning from the terrible accidents that are too frequently recorded, especially in the houses of the working classes, are bringing to the front lamps that are within the reach of all, and are at the same time designed upon true principles with a view to reducing, as far as possible, the risk of accident accompanying their use. In this direction the little lamp that has been sent to us by Messrs. Kiesow and Co. is a happy example. The reservoir is made entirely of metal, furnished with two convenient handles (the value of which is often overlooked); the burner, instead of fitting into the oil-chamber with the usual loose screw, has a simple and efficient bayonet fitting. An ingeniously devised S-shaped tube, attached to the burner, carries the wick down into the body of the reservoir, diminishing to a great extent the danger of the oil escaping in case of the lamp getting overturned. On the whole we consider the lamp to be a good step in the right direction, and hope it will meet with the appreciation it deserves.

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.

Assaying.—Can any of your readers tell me of any book suitable for the practical assaying of such things as brass ashes, zinc ashes, type ashes, tin ashes, &c.? I have "Beringer," but he does not treat of these.—S. J. Habgood.

THE CHEMICAL NEWS.

Vol. LXXII., No. 1872.

THE ACTION OF LIGHT UPON THE SOLUBLE METALLIC IODIDES IN PRESENCE OF CELLULOSE.*

By DOUGLAS J. P. BERRIDGE, B.A., Malvern College.

The action of light upon the metallic iodides appears not to have been thoroughly investigated by any chemist, and, although it has frequently been taken for granted by some experimenters that potassium iodide suffers decomposition when exposed to sunlight, others have passed the subject over in silence, and, so far as I am aware, no text-book upon chemistry mentions the fact. The experiments, an account of which I have to-day to lay before the Section, were commenced in the year 1884, and it was not until eight years later, during most of which interval I had been prevented from finishing my work, that I heard of Videau's investigations; in 1892 I came across a notice of them in Prof. Meldola's book, "The Chemistry of Photography," but as, by a reference to the original paper, I found that Videau had worked upon an altogether different principle from my own, and his results left much to be cleared up, I have continued to prosecute my experiments. Last year a paper was read before the Chemical Society, by Dr. Cook, upon the effect of heat upon iodates and bromates, in the course of which he mentions (*J. Chem. Soc.*, 1894, p. 804) that ordinary purified potassium iodide "liberates iodine when exposed to air and light," but that if the iodide be previously purified by crystallisation from absolute alcohol no such decomposition takes place. Dr. Cook does not mention in his paper the precautions he took to prevent the access of carbon dioxide from the air to his solution, which was contained in a test-tube, and as impurities would be probably more abundant in the open air than in a dark cupboard it seemed to me, after reading his paper, that a more satisfactory method of experiment would be to seal the solution of the iodide in a bulb with a known quantity of air, thus preventing any CO_2 from reaching the liquid and disturbing the results. I may, however, say at once that after doing this my experiments fully confirm Dr. Cook's. Solutions of the so-called pure salt, which, when tested with starch and tartaric acid, gave no immediate colouration, were always decomposed when exposed in sealed tubes containing air to the sunlight; the amount of iodine liberated, however, varied considerably; on the other hand, a solution made with potassium iodide which had been previously fixed with charcoal gave no colouration upon the addition of starch, even after an exposure to sunlight for several weeks.

It is, however, to the decomposition of the iodide in presence of cellulose that I more especially wish to call your attention; in the earlier experiments my method was to saturate a sheet of paper with a solution of the desired iodide, and to expose this to the sunlight in a printing frame under a negative; in my later experiments I have, however, confined myself to the use of sealed bulbs, since by this method only can any quantitative results be obtained. I at first experienced a certain amount of difficulty in obtaining a form of cellulose suited for the purpose, and many experiments in which cotton-wool was used failed, owing to the presence of sodium thiosulphate in the material, from which it could only be removed with great difficulty. When, however, I substituted filter-paper which had been extracted by hydrochloric and hydrofluoric acids for the cotton-wool, much more satisfactory results were obtained. The paper used was that supplied by Schleicher and Schüll, and was in all cases tested for acid, from which it was, however, perfectly free; after reducing a certain quantity of this paper to pulp, and well washing with distilled water, it was introduced into a bulb; the solution of potassium iodide, generally containing a known weight of the salt, was added, and the bulb sealed. After exposure to sunlight the bulbs were opened, a little starch added, and the amount of iodine liberated determined by a centinormal solution of thiosulphate of sodium.

In a typical experiment 85·724 grms. of potassium iodide were dissolved in 500 c.c. of distilled water and five sheets of the pure filter-paper, 12·5 c.m., treated as described, were introduced into a bulb of about 100 c.c. capacity and 50 c.c. of the iodide solution added. In another bulb, of the same size, 50 c.c. of the solution were sealed without the addition of pulp. After an exposure of about four hours to diffused sunlight, the former had acquired a decided reddish colour, whilst the latter remained perfectly colourless; at the end of twenty-five days, during which the bulbs had been exposed in a window, they were opened, when 0·001778 grm. of iodine was found to have been liberated in the former, whilst in the latter only 0·000635 grm. of free iodine was found.

When a solution of half the above strength was used, *i.e.*, one containing 4·286 grms. of potassium iodide dissolved in 50 c.c. of distilled water, the influence of the cellulose was even more marked, for in the bulb containing 50 c.c. of solution and five sheets of extracted paper 0·001524 grm. of free iodine was found, whilst in one containing the same quantity of solution but no pulp, only 0·000191 grm. of iodine had been liberated. In a fifth bulb the same quantity of paper pulp was placed, and the solution of potassium iodide was poured off after the pulp had become thoroughly soaked with it. In this case the liberation of iodine occurred much sooner than in the previous cases, but considerably less was liberated during an exposure of five and twenty days, the total being only 0·000762 grm. The contents of all these five bulbs were tested for alkali with a solution of phenolphthalein; the two in which there was no pulp gave decided colouration with this reagent, whilst the three containing cellulose proved to be quite free from alkali.

In another series of experiments a stronger solution of potassium iodide was used, viz., one containing 76·936 grms. of the salt dissolved in 250 c.c. of water, and this was sealed in bulbs containing a varying quantity of the paper pulp. Four bulbs were taken; in the first, half a sheet of paper reduced to pulp was placed, in the second one sheet, in the third two sheets, and in the fourth four sheets; 40 c.c. of a solution of the strength above described, and therefore containing 12·308 grms. of the salt, were added. These were exposed in a window for ten days, at the end of which time the following results were obtained upon analysis:—

Bulb A.	0·001397	grm. iodine,	trace of	alkali.
" B.	0·001935	"	"	"
" C.	0·002286	"	no free	alkali.
" D.	0·00254	"	"	"

As far as it was possible to judge from the colouration of the pulp, all these bulbs had liberated their maximum quantity of iodine some days before analysis. It will be noticed that the total weight of iodine liberated is very small in the above instances, never exceeding 0·027 per cent of the total iodine present, or 1·120 per cent of the quantity the oxygen in the bulb was able to liberate.

In an experiment made with potassium iodide which had been previously fused with charcoal, about 30 grms. of the salt were fused and dissolved in 100 c.c. of water. 40 c.c. of this solution was sealed in a bulb, and found after twenty-five days to be entirely free from iodine; 50 c.c. were sealed in another bulb with five sheets of paper reduced to pulp, and in this case after the same

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* Read before the British Association (Section B), Ipswich Meeting, 1895.

exposure 0·001651 grm. of free iodine was found, the liquid being free from alkali.

If the air above the iodide solution in the tube is displaced by means of oxygen more iodine is liberated, and the maximum effect seems to be reached earlier; but I have not at present made sufficient experiments to trace any relation between the total quantity of oxygen present and the amount of iodide decomposed. Hydrogen, on the other hand, reduces the quantity of I_2 liberated, and if the oxygen is entirely removed from both the bulb and the solution I have no doubt that the iodide would remain perfectly undecomposed, although at present I have not succeeded in obtaining this theoretical result.

The equation for the reaction is most simply written:—

$$2KI+H_2O+O=2KOH+I_2.$$

I hope to show presently that this does not completely represent the reaction, but, allowing that it gives the first stage of the decomposition, the reason for the very marked increase in the quantity of iodine liberated when cellulose is present becomes apparent, for the iodine set free by the above reaction should, and doubtless to a considerable extent does, re-combine with the potassium hydrates formed, producing a mixture of iodide and iodate. If, however, any substance is present which will combine with the alkali, removing it from the sphere of action, the oxidation is enabled to proceed without the subsequent combination of the liberated iodine. The absence of alkali in the solutions containing sufficient cellulose, and its presence when cellulose is either absent or present in small quantities, seems conclusive evidence that the increase in the amount of the iodide decomposed in presence of this substance is due to the removal of the alkali.

In order to obtain prints on paper by the decomposition of potassium iodide, I at first used a frame like that sold in toy-shops as a drawing-slate; more recently, however, I have used one exactly like the ordinary photographic printing-frames. The paper must not be too absorbent, and one with a smooth surface answers best; although I have been able to obtain fine proofs from ordinary negatives, the detail is too rough for these to be satisfactory, and consequently I have generally employed a negative made by cutting out a device in paper, fastening this to a sheet of glass, and varnishing. The best strength for the solution appears to be one containing about 1 part of the salt dissolved in 8 parts of water, a weaker solution requiring a much longer exposure, whilst if a stronger solution is used the ground of the resulting print is apt to become too dark. If a sheet of note-paper is moistened with the solution, and at once placed in the frame, it will, in about five minutes in diffused daylight, become printed in a light chocolate and pink colour, with the device cut out of the negative; if the exposure is prolonged the colour becomes much darker, and at the same time, owing to the spontaneous decomposition of the salt, the parts unexposed to the light become more or less deeply tinted; the exposed part is, however, always so much darker than the rest that the print stands out well. If the paper is allowed to dry in the dark after being saturated, it assumes a faint chocolate tint, and when placed in the frame and exposed for about four hours becomes printed in a dark chocolate, although it shows no signs of darkening for some time after a similar sheet of damp paper has become deeply marked. If a piece of paper, after being printed to a chocolate colour, is moistened with water, the colour of the print at once changes from chocolate to blue, and even if it is still damp when removed from the printing-frame the colour is never blue until water has been added to it. In order to arrive at some definite conclusion concerning the nature of the change occurring, I attempted, by means of a solution of iodine, to imitate the colour produced during exposure of the saturated paper to light; using at first a solution of iodine in an aqueous one of potassium iodide, I obtained, when it was poured over a sheet of writing-paper, a stain which varied according to the concentration of the solution from blue to bluish-black; even when the solution was so dilute that in some lights it was difficult to see any mark, the stain upon the paper was always blue. I next used solutions of the element in benzene, carbon disulphide, chloroform, and alcohol: when these solutions were poured over paper, stains were produced which varied with the strength of solution from yellowish-brown to walnut. In other words, whilst the colour of the exposed paper was always tinged with pink in all attempts to imitate this, I obtained a blue colour if I used an aqueous, or a yellow colour if I used an anhydrous, solution of iodine.

I may here mention that all the note-paper I have examined contained starch, and that this solution only produces the well-known so-called iodide of starch in the presence of water; this latter fact may be shown by passing an anhydrous solution of iodide over paper coated with starch, when a brown stain is produced, which becomes blue, however, upon the addition to it of water. This explained the difference in the colour of the stains produced in the various solutions of iodine, but it did not help to indicate the action of light upon the potassium iodide; in fact, it made it rather more difficult, as it appeared to show that the colour of the prints was not due to the presence of free iodine; the only probable conclusion was, therefore, that the iodine combined at the moment of liberation with the still unaltered potassium salt, forming the tri-iodide or some similar compound. If this compound colours paper a pinkish chocolate, and is decomposed into its constituents by water, an explanation is at hand to account for the observed phenomena. To test whether this was the case, a little iodine was added to a solution of starch, and to the blue liquid thus obtained a concentrated solution of potassium iodide was added; the colour, however, remained unaltered, and after a large number of experiments I came to the conclusion that the amount of water necessary to bring the starch into solution was more than enough to decompose any higher iodide which might be found; the experiment was therefore varied by adding to a piece of solid starch which had been coloured pink by the addition of iodine in alcoholic solution a few drops of a saturated solution of potassium iodide; the colour of the starch deepened, but did not turn blue. I then took a piece of paper which was coloured blue by the presence of a small quantity of starch iodide, and added to it a very concentrated solution of potassium iodide; the blue colour changed to one approximating very closely indeed to that obtained by the action of light upon the iodised paper. This experiment seemed to justify the hypothesis that the colour of a piece of iodised paper after exposure is due to the presence of potassium tri-iodide or some similar compound.

In order to fix a print obtained upon the iodised paper, it is washed for a short time in running water; if the washing be too long continued, or if the paper be allowed to remain in a dish of water, the iodine dissolves and the proof is, of course, lost; lead acetate in very dilute solution is now poured over the paper, which is then again washed. If the print fixed in this manner is left it will begin at once to fade, and in a few days, or even hours, no trace of the design will be visible; if, however, a coat of size is put over it, and this followed by one of a hard varnish, the stability of the print is very much increased, and I have specimens which are more than three years old and are still distinct.

I have up to this point mentioned only the behaviour of potassium iodide when exposed to light, as the salt is the most easily obtained in a comparatively pure condition; it is the one with which I have chiefly worked. I have, however, made qualitative experiments upon the iodides of sodium, calcium, strontium, barium, zinc, cadmium, and iron.

Sodium iodide was bought as pure, and was probably no more impure than the ordinary potassium salt; it yielded a print of the same depth of colour as that obtained from potassium iodide in considerably less time. As far, however, as could be judged from qualitative experiments, the maximum iodine was liberated about the same in each case.

Calcium, strontium, and barium iodides were obtained by adding the metallic carbonate to hydriodic acid which was free from iodine; the solutions, after filtering, were neutral and gave no colouration with starch.

Barium iodide gave a decided print in about ten minutes, and after an exposure of about two hours a strong print was obtained, which was, as in the case of the potassium salt, at first chocolate-coloured, turning blue on the addition of water.

Strontium iodide appears to be more sensitive to the action of light than the barium salt, a strongly-coloured proof being obtained after an exposure of about an hour.

Calcium iodide appears to be even more sensitive to the light than the strontium salt; in fact, the amount of iodine liberated seemed to vary roughly inversely as the atomic weight of the metal with which it is combined. I have experiments now in progress with a view to testing this.

Zinc iodide was obtained by placing 4 grms. of iodine in a flask together with metallic zinc and a little water. After standing in a warm place for a couple of days, the colour of the solution was discharged and when filtered and at once tested for iodine, it proved to be free from this element. The solution was made up to about 50 c.c., and paper was saturated with it as in the previous experiments. In all cases distinct proofs were obtained, but as the solution is exceedingly unstable, the unexposed portions were much discoloured, making the device more difficult to read.

Ferrous iodide was obtained in a similar manner to the zinc salt; iron-filings and iodine being warmed together, the filtered liquid was colourless, and gave no colouration with starch. It is, apparently, less sensitive to the action of light than the other soluble iodides, but I have obtained distinct prints when using it. The exposed parts are, of course, as in the case of the zinc salt, much discoloured owing to the spontaneous decomposition of the compound.

Cadmium iodide differs from all the other iodides I have examined, inasmuch as it gives a blue and not a pink print, it would thus appear that this element alone is unable to form a higher iodide.

THE RESPIRABILITY OF AIR IN WHICH A CANDLE-FLAME HAS BURNT UNTIL IT IS EXTINGUISHED.*

By FRANK CLOWES, D Sc.

At the last meeting of the British Association the author stated the composition of artificial mixtures of nitrogen and of carbon dioxide with air, which were just able to extinguish various flames. It was found that the flames of ordinary candles and lamps were extinguished by mixtures which contained on an average about 16·5 per cent of oxygen and 83·5 per cent of the extinctive gases. A flame of coal gas, however, required for its extinction a mixture still poorer in oxygen, and containing 11·3 per cent of oxygen and 88·7 per cent of the extinctive gases. These results have since been confirmed by a different method.

The method consisted in allowing the flames to burn in air inclosed over mercury until they were extinguished; the remaining extinctive atmosphere was then subjected to analysis, when its composition was found to be practically identical with that previously obtained from the artificial mixtures. An analysis of air expired from the lungs proved that it was also of the same composition as that which extinguished the flame of an ordinary candle or lamp.

The average percentage composition of expired air and of air which extinguishes a candle-flame is as follows:—Oxygen, 15·9; nitrogen, 80·4; carbon dioxide, 3·7.

Now an atmosphere of this composition is undoubtedly respirable. Physiologists state that air may be breathed until its oxygen is reduced to 10 per cent. The maximum amount of carbon dioxide which may be present is open to question, but it is undoubtedly considerably higher than 3 per cent. Dr. Haldane maintains that the above atmosphere is not only respirable, but would be breathed by a healthy person without inconvenience of any kind; he further states that no permanent injury would result from breathing such an atmosphere for some time.

The conclusion to be drawn from these facts is, that an atmosphere must not be considered to be dangerous and irrespirable because the flame of an ordinary candle or oil-lamp is extinguished by it. The view is very generally advanced that a man must on no account venture into air which extinguishes the flame of a candle or of a bundle of shavings. It will be seen that this precaution may deter one from entering an atmosphere which is perfectly safe and respirable, and from doing duty of a humane or necessary character.

An atmosphere which extinguishes a coal-gas flame, however, appears to approach closely to the limit of respirability, as far as the proportion of oxygen which it contains is concerned. Hence the coal-gas flame appears to be a more trustworthy indicator of respirability than the flame of a candle or oil-lamp.

Undoubtedly the candle and lamp flames should be discarded as absolute tests of respirability of air.

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[*] Read before the British Association (Section B), Ipswich Meeting, 1895.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

[The complete works of the late J. S. Stas have recently been published at Brussels. They contain several memoirs on important points of chemistry and physics which are there published for the first time. Among these none equal in interest that entitled " Recherches Chimiques et Etudes Spectroscopiques sur différents Corps Simples." In the following pages we commence the translation of this memoir, and we propose to continue its publication from week to week till completed].

Chapter I.

Chemical Researches and Spectroscopic Studies of Sodium, Potassium, Lithium, Calcium, Strontium, Barium, and Thallium.

Introduction.

In undertaking these chemical works and spectroscopic studies, my object was to ascertain whether I could cause, by increasing the temperature or the intensity of the electric current, and contrary to what is generally admitted, a correlation among the characteristic bands of the luminous spectra of compounds of sodium, potassium, lithium, calcium, strontium, barium, and thallium, in such a state of purity as the improvements in the methods of chemical analysis permit me to actually obtain these bodies.

I was well aware that if my experiments failed, after having taken great pains and having devoted to this work an amount of time which I might perhaps have used more profitably, I should add nothing to the sum of our *spectroscopic* knowledge. Still, I should free science from an hypothesis which has led astray, and may again lead astray, many clever men; it seemed to me that this was just as much helping to advance *real* knowledge.

Chemical analysis is generally recognised as being unable to detect the presence of sodium, still less to find the percentage of this metal, when it exists in a very small proportion in a given compound.

Since the memorable works of Messrs. Bunsen and Kirchhoff on spectrum analysis, chemists have almost invariably used this method of detecting the presence of sodium.

Whilst applying their method to the examination of soluble compounds obtained by *the method of fractional crystallisations*, the illustrious authors have found that, by this process, one can never entirely separate the sodium from the body with which it is mixed; one must employ simultaneously a chemical reaction by which one can obtain an absolute separation. M. Bunsen and then M. Diehl were the first to practise this method, the latter on the advice of his illustrious master.

The occurrence of the sodium line in the spectrum of nearly all compounds led Mr. Lockyer to believe that this metal is evolved by the dissociation of the elements of the bodies on which one is working. This hypothesis, if it were verified, would necessitate the overthrow of all the fundamental notions of the physico-chemical sciences.

However improbable it has appeared, as regards the majority of chemists who have done accurate work, the name of Mr. Lockyer, and the brilliant services which he has rendered to science by his spectroscopic researches, have induced me to submit his hypothesis to a critical examination, about which he has done me the honour of writing to me (1878).

The work that I have undertaken with potassium has also had as an object the solving by its means the problem of ascertaining if it is really possible to procure a chloride of potassium which does not give, under any circumstances, any indication of the presence of sodium, and of obtaining this compound in such a state of purity, that the result arrived at in determining its atomic weight in regard to that of silver would leave no doubt in anybody's mind.

My investigations have included the compounds of potassium, sodium, thallium, lithium, calcium, strontium, and barium.

I have borne in mind the fact that the results depend as much on the medium in which the metallic compounds are enclosed, as on their *accidental impurities*.

This medium being, for example, air, I have found or I have not found sodium, according as the air gives or does not give indications of the presence of this metal. This fact has led me to examine the air by means of the spectroscope.

Respecting the Characteristics Impressed by the Surrounding Air on Hydrogen Flames, Illuminating Gas, Hydrogen Blowpipe Flame, Oxy-hydrogen Blowpipe Flame, Oxy-carbo-hydrogen Blowpipe Flame, and Ordinary Flame, and on the Electric Discharge and Electric Arc.

I must commence my statement with the observations which I have made on air.

What I am about to say relates exclusively to the air of Brussels, to that in the "Musée de l'Industrie," where I have worked, and in my own laboratory. Amongst the observations which I have to mention are many familiar to chemists engaged in spectrum analysis; but I must recapitulate them in order to make my statement as complete as possible.

The room in the Musée de l'Industrie in which I have carried on my spectroscopic researches measures about 1143 cubic metres. It can be made into a dark room, as I have had occasion to do daily during my researches.

During the time occupied by my work the room was placed entirely at my disposal.

When the *external* air is quiescent, and has been for several days saturated with moisture, a state of things which occurs in Brussels from the end of October to the middle of December, and the room, previously washed out with a copious supply of water, and properly ventilated from the external saturated atmosphere, has been kept closed for twelve or eighteen hours, a time necessary for the deposition of particles of dust, mineral matters, &c., the jet of gas, mingled with a suitable supply of air, issuing from a well made Bunsen burner, terminated by a pipe of platinum, silver, or gold, free from sodium, or even a pipe of brass, well cleansed inside and out, burns with a flame of pure rich blue, in which it is impossible to detect the presence of sodium by any spectroscope. Let one then make a prismatic analysis of the top, middle, and base of the luminous cone, the diameter of which varies from 1 to 1½ c.m. and the height from 10 to 25 c.m.

If one introduces, by means of a loop of fine platinum wire, into the middle of the height of the flame, some dilute hydrochloric acid or some pure chloride of ammonium, the colour of the upper half changes immediately; it turns green, and the intensity of the colour varies in proportion to the quantity of hydrochloric acid or chloride of ammonium introduced. In the flame thus rendered visible, it is impossible to recognise by prismatic analysis the slightest trace of the spectrum of sodium, or of a partially burnt hydrocarbon.

Having substituted for the Bunsen burner a blowpipe of platinum or silver, previously cleansed from all sodium particles, and for the illuminating gas properly purified hydrogen, one notices that this gas burns in pure air with a flame so colourless, and with such a faint luminosity, that in the dark the eye can scarcely perceive it. One cannot discern in any part of this flame the slightest indication of the sodium "D" line, or of a continuous spectrum.

The introduction of hydrochloric acid or of pure ammonia into hydrogen burning in pure air, gives directly to its colourless flame a tint of a livid greenish yellow, similar to that seen when burning hydrogen in chlorine. The prismatic analysis of this flame does not enable one to detect the presence of the sodium line or of a continuous spectrum.

In the blowpipe, with a pipe of pure platinum, cleansed inside and out from sodium particles, fed with a mixture in proper proportions of illuminating gas, or of hydrogen and air, or of pure hydrogen and oxygen, spectroscopic observation demonstrates in all cases the complete absence of the sodium "D" line, whatever may be the part of the flame examined. After the introduction of hydrochloric acid, which greatly alters the colour of these flames, one can find no trace of the sodium line.

To complete these proofs, I must add that, in the darkened room, with pure air, spectrum analysis does not enable one to detect the appearance of any spectrum, not even a glimmer from the upper two-thirds of a flame from a well made Bunsen burner,* terminated by a platinum tube, or from a flame of from 10 to 25 c.m. length issuing from a platinum blowpipe supplied with air or with pure oxygen.

The spectrum only appears from this part of the flame or blowpipe flame when one puts there a solid non-volatile body, and in this case the spectrum produced is continuous, as we know.

As regards the blowpipe flame which results from the combustion of an excess of pure hydrogen in equally pure oxygen issuing under pressure from a platinum burner, frequent observations permit me to state that, in the portions of this flame where the temperature is not high

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* When the burner is faultily made, as is often the case, the flame, instead of consisting of a *single cone* surrounded by a barely visible but very hot envelope, resolves itself into two cones, extending from the base almost to the apex; an internal cone, slightly luminous and *purple*, surmounted by a second cone of *pure blue* in pure air, surrounded again by a barely visible envelope where the combustion of carbon takes place. In the flame from this badly-made burner, the second cone agrees with the conditions mentioned above; that is, in the absence of any spectrum, although the inside cone gives to spectrum analysis the partial spectrum of burning hydrocarbons, to which I shall return later on. *Whichever was the burner used, I have always placed in the barely visible external envelope of the flame the body which I wished to put in it for the purpose of making a spectrum analysis.*

enough to bring the platinum well up to melting-point, spectrum analysis does *not* enable me to see a spectrum. The place of the spectrum is occupied entirely by a dark band, even when the width of the slit in the collimator of the spectroscope exceeds the limit necessary for distinct vision of the dark lines in the solar spectrum. As soon as the temperature of the flame reaches the fusing-point of platinum, the hydrogen becomes incandescent; its colour becomes a pale or sky blue. Spectrum analysis then shows the appearance of a continuous spectrum, yet without the formation of bands or lines. It resembles that from the upper third of a blowpipe flame in which the hydrogen has not reached the point of incandescence. As a matter of fact, the flame which issues from an oxyhydrogen burner under more or less pressure, is composed of two cones superposed, as in the case of a badly made Bunsen burner, of a lower internal cone coloured light blue in pure air, merging into the upper colourless cone, when it consists of the oxyhydrogen flame fed with an excess of hydrogen and oxygen.

Spectrum analysis of this lower internal cone gives a continuous spectrum, destitute of bands or lines, and whose brightness increases continuously from the point up to the part where the temperature is at a maximum and in a condition to keep iridium and rhodium fused. I shall return later on to the subject.

On substituting for the hydrogen some illuminating gas or a very volatile hydrocarbon,—for instance, petroleum naphtha or similar body in the state of vapour, issuing from a platinum burner,—one notices analogous facts as regards the lower cone, which is always coloured blue. The spectrum analysis of this cone allows one to see a continuous spectrum crossed with bands and lines of exceeding brilliance. The bands and lines are numerous. Towards the portion of the lower cone, where the light of the spectrum is most dazzling, the temperature is so high that rhodium and iridium can be kept fused. I shall return to this spectrum later on.

To resume—If one makes a prismatic analysis of that part of the blowpipe flame of hydrogen and air, of oxyhydrogen, or of oxyhydrocarbon, in which platinum begins to melt or in which it is quite melted, or in which iridium can be kept in a state of fusion, whether there be either no spectrum or one of great brilliance; in any case the spectrum analysis does not enable one to detect the presence of the sodium D line, when the air in which the experiment takes place is pure, or at least has a given relative degree of purity; when the elements used to produce the flame are pure; and, lastly, when the apparatus itself yields no trace of sodium.

I shall certainly not surprise those who have done any spectrum analysis when I say that I have met with the greatest difficulties in verifying, under the conditions given, the facts written above, simple as they seem.

(To be continued).

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.*

By F. W. CLARKE.

(Concluded from p. 167).

Thallium.

Two determinations of atomic weight were made by Wells and Penfield to ascertain the constancy of the element as such (*Am. Journ. Sci.*, 3, xlvii., 466). The nitrate was fractionally crystallised until about 1-20th remained in the mother-liquor, while another twentieth had been subjected to repeated re-crystallisation. Both fractions were converted into thallium chloride, which was dried at 100°, and in both the chlorine was estimated by weighing as silver chloride on a Gooch filter. The results were as follows:—

	TlCl.	AgCl.	At. wt. Tl.
Crystals	3·9146	2·3393	204·47
Mother-liquor ..	3·3415	1·9968	204·47

Calculated with Ag = 107·92 and Cl = 35·45.

In the report for 1893 Lepierre's work on thallium was given, and the last value cited was Tl = 203·00, varying widely from the rest of the series and affecting the mean. The mean stated by Lepierre was 203·62, and as found by me was 203·57. Lepierre (*Bull. Soc. Chim.*, 3, xi., 423) now calls attention to the fact that his value 203·00 was a misprint for 203·60, and that his mean was therefore correctly given. He also gives additional details relative to his work.

Bismuth.

The long-standing controversy between Schneider and Classen over the atomic weight of bismuth has led to a new set of determinations on the part of Schneider (*Journ. Prakt. Chem.*, 2, l., 461). The old method was still used; namely, of converting the metal into the trioxide by means of nitric acid and subsequent ignition of the nitrate; but the metal itself was carefully purified. Results as follows:—

Wt. Bi.	Wt. Bi_2O_3.	P.c. Bi in Bi_2O_3.
5·0092	5·5868	89·661
3·6779	4·1016	89·648
7·2493	8·0854	89·659
9·2470	10·3142	89·662
6·0945	6·7979	89·653
12·1588	13·5610	89·660
	Mean ..	89·657

If O = 16, Bi ranges from 207·94 to 208·15, or in mean 208·05, confirming the earlier determinations.

Tin.

Incidentally to his paper on the white tin sulphide Schmidt gives one determination of the atomic weight of the metal (*Ber. d. Chem. Ges.*, xxvii., 2743).

0·5243 grm. Sn gave 0·6659 SnO_2. Hence Sn = 118·48.

Anomalous Nitrogen.

An important discovery has been made by Lord Rayleigh, who finds that nitrogen obtained by purely chemical methods is perceptibly lighter than that from atmospheric air (Chem. News, lxix., 231, May 18, 1894). Equal volumes of the gas, variously prepared, weighed as follows:—

By passing NO over hot iron	2·30008
,, N_2O ,, ...	2·29904
,, $AmNO_2$,, ...	2·29869

For nitrogen from air he found:—

From air passed over hot iron	2·31003
,, ,, through moist FeO_2H_2	2·31020
,, ,, over hot copper	2·31026

Investigating the cause of this anomaly, with the cooperation of Ramsay, Rayleigh came to the astonishing results communicated a few months later to the British Association. It was found, in short, that atmospheric air contains a gas heavier than nitrogen, and hitherto unknown. Its density, in a sample as pure as could be obtained, was 19·09, and it was characterised by extraordinary inertness. Whether it is a new element, or allotropic nitrogen, N_3, remains to be determined. The work is cited here because it shows that the density of nitrogen as hitherto determined can give no trustworthy value for the atomic weight of the element.

Miscellaneous Notes.

Some data bearing upon the atomic weight of tellurium are given by Gooch and Howland (*Am. J. Sci.* [3],

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* From the *Journal of the American Chemical Society*, vol. xvii., No. 3. Read at the Boston Meeting, Dec. 28, 1894.

xlviii., 375). As the homogeneity of tellurium is still uncertain, I omit their details.

Wanklyn's attempt to show that the atomic weight of carbon is not 12, but 6, was noted last year. He has since published more on the subject in a paper on Russian Kerosene (*Phil. Mag.*, [5], xxxvii., 495), and the matter was also discussed at the Oxford meeting of the British Association (Chem. News, lxx., 87, Aug. 24, 1894).

In a communication upon the Stasian determinations (*Compt. Rend.*, cxviii., 528), Hinrichs discusses the availability of silver as a secondary standard in the scale of atomic weights. He makes silver, chlorine, bromine, iodine, and sulphur all Proutian in value. Hinrichs also has published his views upon atomic weights *in extenso* in book form ("The True Atomic Weight of the Chemical Elements, and the Unity of Matter," by Gustavus Detlef Hinrichs, St. Louis, 1894).

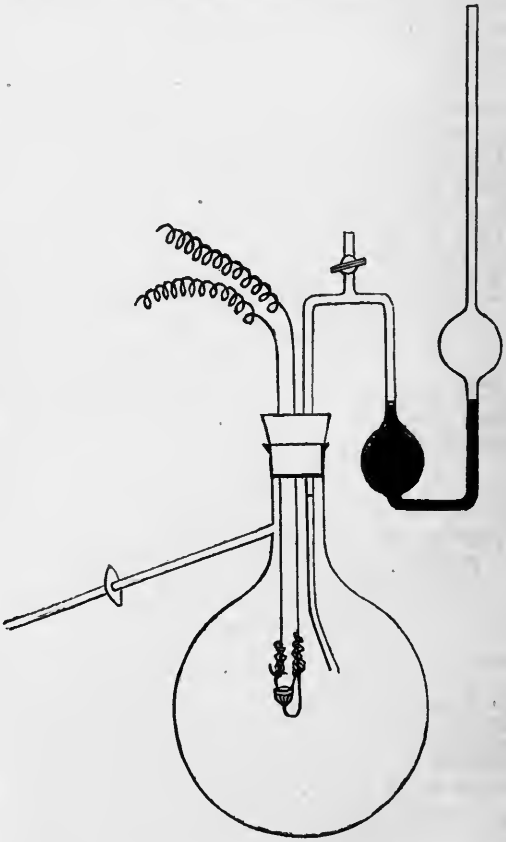
In conclusion I submit a table of atomic weights revised to January 1, 1894. O = 16 is still retained as the base of the system; but I hope that in another year it will be practicable to return to H = 1.

Name.	Atomic weight.
Aluminium	27·
Antimony	120·
Arsenic	75·
Barium	137·43
Bismuth	208·
Boron	11·
Bromine	79·95
Cadmium	112·
Cæsium	132·9
Calcium	40·
Carbon	12·
Cerium	140·2
Chlorine	35·45
Chromium	52·1
Cobalt	59·5
Columbium	94·
Copper	63·6
Erbium	166·3
Fluorine	19·
Gadolinium	156·1
Gallium	69·
Germanium	72·3
Glucinum	9·
Gold	197·3
Hydrogen	1·008
Indium	113·7
Iodine	126·85
Iridium	193·1
Iron	56·
Lanthanum	138·2
Lead	206·95
Lithium	7·02
Magnesium	24·3
Manganese	55·
Mercury	200·
Molybdenum	96·
Neodymium	140·5
Nickel	58·7
Nitrogen	14·03
Osmium	190·8
Oxygen	16·
Palladium	106·5
Phosphorus	31·
Platinum	195·
Potassium	39·11
Praseodymium	143·5
Rhodium	103·
Rubidium	85·5
Ruthenium	101·6
Samarium	150·
Scandium	44·
Selenium	79·
Silicon	28·4
Silver	107·92
Sodium	23·05
Strontium	87·66
Sulphur	32·06
Tantalum	182·6
Tellurium	125·
Terbium	160·
Thallium	204·18
Thorium	232·6
Thulium	170·7
Tin	119·
Titanium	48·
Tungsten	184·9
Uranium	239·6
Vanadium	51·4
Ytterbium	173·
Yttrium	89·1
Zinc	65·3
Zirconium	90·6

LECTURE APPARATUS.

By Dr. W. R. HODGKINSON, F.R.S.E.

In the *Annalen der Chemie* (vol. cclxxxiv., p. 3) Volhard describes an apparatus for certain lecture purposes. I have had an apparatus of very similar form and for the same purposes in use in my lectures at the Royal Military Academy for the past eight years or more.



One or two additions or improvements were added some time ago by my assistant, Mr. J. Young, A.R.C.S.

The substance to be burnt can be fired by the electric wires; the particular form of gauge obviates any danger of gases escaping owing to excessive expansion at the moment of burning. It is, as will be seen, only a large distilling flask with a stopcock sealed on the tube. Oxygen may be driven in and through by means of the two taps, *after* the substance has been put in the cup. This is an advantage generally.

As a rule the rubber stopper is wired down and mercury used in the gauge.

The apparatus can be used in a rough quantitative way.

Royal Military College, Woolwich.

ON THE
CONSTITUENTS OF THE GAS IN CLEVEITE.
By C. RUNGE and F. PASCHEN.

WE have investigated the spectrum of the gas discovered in the mineral clèveite by Ramsay, and have found it to be most regular. It consists of six series of lines, the intensity of the lines in each series decreasing with decreasing wave-lengths. Similar series of lines have been observed in many spectra. The first series was discovered by Dr. Huggins in the ultra-violet spectra of a number of stars. It proved to belong to hydrogen, and to be the continuation of the four strong hydrogen lines in the visible part of the spectrum. Johnstone Stoney had already shown that three of the wave-lengths of the visible hydrogen lines were most accurately proportional to the values 9/5, 4/3, 9/8, when Balmer discovered that these values were given by the formula—

$$\frac{m^2}{m^2-4},$$

for $m = 3, 4, 6$, and that the other wave-lengths of the series were proportional to the values obtained by substiting for m the other entire numbers greater than three. The series has now been followed from $m=3$ to $m=20$, the lines growing weaker and weaker to the more refrangible side, and approaching each other closer and closer. The formula shows that they approacb a definite limit for large values of m. This is seen more clearly when we consider wave-numbers instead of wave-lengths, which according to the formula would be proportional to—

$$1 - \frac{4}{m} 2.$$

Many series of lines similar to the hydrogen series were discovered by Liveing and Dewar. They have called them harmonic series, and have compared them to the series of over-tones of a vibrating body. They have been further studied by Rydberg and by Kayser and Runge. We cannot here enter into any detailed account. We only want to explain so much as to make the conclusions understood which we have drawn from the spectrum of the gas in clèveite. The wave-lengths λ of the lines belonging to the same series are always approximately connected by a formula somewhat similar to Balmer's—

$$1/\lambda = A - B/m^2 - C/m^4.$$

A determines the end of the series towards which the lines approach for high values of m, but does not influence the difference of wave-numbers of any two lines. B has nearly the same value for all the series observed, and C may be said to determine the spread of the series, corresponding intervals between the wave-numbers being larger for larger values of C. As B is approximately known, two wave-lengths of a series suffice to determine the constants A and C, and thus to calculate approximately the wave-lengths of the other lines. It was by this means that we succeeded in disentangling the spectrum of the gas in clèveite, and showing its regularity.

In the spectrum of many elements two series have been observed for which A has the same value, so that they both approach to the same limit. In all these cases the series for which C has the smaller value, that is to say which has the smaller spread, is the stronger of the two. In the spectrum of the gas in clèveite we have two instances of the same occurrence. One of the two pairs of series, the one to which the strong yellow double line belongs, consists throughout of double lines whose wave-numbers seem to have the same difference, while the lines of the other pair of series appear to be all single. Lithium is an instance of a pair of series of single lines approaching to the same limit. But there are also many instances of two series of double lines of equal difference of wave-numbers ending at the same place as sodium, potassium, aluminium, &c. There are also cases where the members of each series consist of triplets of the same difference of wave-numbers as in the spectrum of magnesium, calcium, strontium, zinc, cadmium, mercury. But there is no instance of an element whose spectrum contains two pairs of series ending at the same place. This suggested to us the idea that the two pairs of series belonged to different elements. One of the two pairs being by far the stronger, we assume that the stronger one of the two remaining series belongs to the same element as the stronger pair. We thus get two spectra consisting of three series each, two series ending at the same place, and the third leaping over the first two in large bounds and ending in the more refrangible part of the spectrum. This third series we suppose to be analogous to the so-called principal series in the spectra of the alkalis, which show the same features. It is not impossible, one may even say not unlikely, that there are principal series in the spectra of the other elements. But so far they have not been shown to exist.

Each of our two spectra now shows a close analogy to the spectra of the alkalis.

We therefore believe the gas in clèveite to consist of two, and not more than two, constituents. We propose to call only one of the constituents helium, the one to which the bright yellow double line belongs, whose spectrum altogether is the stronger one, while the other constituent ought to receive a new name.

We have confirmed this rather hypothetical conclusion by the following experiment:—The connection leading from our supply of clèveite gas to the vacuum tube contained a side branch parting from it and joining it again. There were stopcocks on either side of the side branch, and a third one in the side branch. In the main tube between the ends of the side branch a plug of asbestos was tightly inserted. To prepare the vacuum tube only the tap leading to the supply was closed, the whole space up to this tap being carefully evacuated. Now the side branch was closed, and the tap leading to the supply was opened. Then we observed that the light of the electric discharge in the vacuum tube was at first greenish, and after a while grew yellow. By cutting off the current of gas after a sufficiently short time, we succeeded in making a vacuum tube which remained greenish. On examining it in a small spectroscope with which we could overlook the whole spectrum, we found that the intensities of the lines had changed. The yellow line was scarcely as bright as the green line 5016, and the red line 7065 had apparently decreased relatively to 7282 and 6678, although it was still stronger than 7282. The two lines that had decreased in intensity belong to the second set of series, while the others are members of the first set. The other visual lines of the second set could not very well be examined, because they are more in the violet part.

This observation confirms our spectroscopic result. The gas in clèveite may be taken to be a mixture of two gases of different density, of which the lighter one is more rapidly transmitted through the plug of asbestos. There is, however, the objection to be raised, that in the green tube the pressure is less, and that the difference of intensities is due to the pressure being different. This must be further inquired into.

We were not satisfied with the visual observation of the change of intensities in our green tube, but thought it desirable to test the conclusion by the bolometric measurement of the two lines that we have discovered in the ultra-red part of the spectrum. If we were right, the ultra-red line of smaller wave-length, which belongs to the second set of series, ought to have decreased in intensity relatively to the other ultra-red line. This we found to be so indeed. In the yellow tubes the intensity of the smaller wave-length was to that of the other on an average as 3 to 1, while in the green tubes it was as 1·8 to 1. This confirmation we consider the more valuable as it does not depend on any estimation which may be biassed by the personal opinion of the observer, but is based on an objective numerical determination.

Another confirmation may be gathered from the spectrum of the sun's limb and that of several stars. Let us confine our attention to the six strongest lines in the visible part of the spectrum:—

7066, 6678, 5876, 5016, 4922, 4472.

The first, third, and sixth belong to the second set of series; the second, fourth, and fifth to the first set. These six lines have all been observed in the spectrum of the sun's limb, as Norman Lockyer and Deslandres have pointed out. Now, according to their appearance in the spectrum of the sun's limb, they may be classed in two groups, one group being always present, the other group being sometimes present. C. A. Young long ago called attention to the difference in the frequency of appearance of the chromospheric lines. He has given them frequency numbers, roughly estimating the percentage of frequency with which the lines were seen during the six weeks of observation at Sherman in the summer of 1872. According to Young, 7066, 5876, 4472 have the frequency number 100, while 6678, 5016, 4922 have the numbers 25, 30, 30, showing that one of the two constituents was always present, while the other was only seen about once in every four cases.

The lines of both constituents have been observed in the spectra of a considerable number of stars, β, δ, ε, ζ, γ Orionis, α Virginis, β Persei, β Tauri, η Ursæ majoris, β Lyræ. In the spectrum of β Lyræ thirteen lines have been identified with certainty. But the most interesting case in point is the spectrum of Nova Aurigæ, that wonderful star whose sudden appearance was announced to astronomers in 1892 by an anonymous post-card. In the spectrum of Nova Aurigæ the two lines 5016 and 4922 were very strong, while 4472 was weak, and 5876 has only been seen by Dr. Huggins, we believe only on one occasion, and appears to have been very weak. Now 5016 and 4922 belong to the lighter constituent, and are together with 6678 the strongest lines in the visible part of the spectrum; while 5876 and 4472 are the strongest lines of the other constituent in the visible part of the spectrum. In Nova Aurigæ, therefore, the lighter constituent gave a much brighter spectrum than helium proper. But there may here be raised an objection, which indeed we do no not know how to refute. Why has the line 6678 not been observed? It is a pity that the red part of the spectrum cannot be more easily photographed. Nova Aurigæ has now become very weak, and besides the spectrum is quite altered, so that we shall never know whether the red line 6678 was really absent or has only escaped notice.

From the fact that the second set of series is on the whole situated more to the refrangible part of the spectrum, one may, independently of the diffusion experiment, conclude that the element corresponding to the second set is the heavier of the two. In the spectra of chemically related elements like Li, Na, K, Rb, Cs, or Mg, Ca, Sr, or Zn, Cd, Hg, the series shift to the less refrangible side with increasing atomic weight. But it appears that in the spectra of elements following each other in the order of their atomic weights in a row of the periodic system like—

Na, Mg, Al;
K, Ca;
Cu, Zn;
Rb, Sr;
Ag, Cd, In;

the series shift the opposite way, so that the spectrum of the element of greater atomic weight is as a whole situated further to the more refrangible side. Now in our case the density of the gas has been determined by Langlet (published by Clève) and by Ramsay to be about double the density of hydrogen. Assuming the atomic weights of the two constituents to be between that of lithium and that of hydrogen, they would both belong to the same row of the periodic system, and therefore the more refrangible set of series would correspond to the greater atomic weight.

For convenience of reference all the observed lines are given in the following table, the wave-lengths being abridged to tenth-metres.

Lighter Constituent.

Principal series.	First subordinate series.	Second subordinate series.
20400	6678	7282
5016	4922	5048
3965	4388	4438
3614	4144	4169
3448	4009	4024
3355	3927	3936
3297	3872	3878
3258	3834	3838
3231	3806	3808
3213	3785	

Heavier Constituent (Helium proper).

	Double lines.	Double lines.
11220	5876	7066
3889	4472	4713
3188	4026	4121
2945	3820	3868
2829	3705	3733
2764	3634	3652
2723	3587	3599
2696	3555	3563
2677	3531	3537
	3513	3517
	3499	3503
	3488	3491
	3479	3482
	3472	
	3466	
	3461	

—*Nature*, September 26, 1895.

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Continued from p. 170).

Calculation of Results.

In the calculations it is assumed that the laws of perfect or ideal gases may be applied to the mixtures of vapours; that is, the laws of Boyle, Gay-Lussac, and Dalton. Where not too much vapour is present in the gaseous mixture the legitimacy of this assumption is unquestionable; and even though this condition be not fulfilled, the

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* Abridged from the *Journal of the American Chemical Society* vol. xvii., No. 8, August, 1895.

Table I.—*Vapour-tensions of Pure Liquids.*

Name of liquid.	Temperature.	Loss in grms.	Volume of loss in c.c.	Volume of air in c.c.	Internal pressure in m.m. Hg.	Barometer in m.m. Hg.	Tension of vapour in m.m. Hg.	Tension according to other observers.
Benzene	34·8°	1·3805	443·	1876	5	760	145·4	147·2 (Y)
Monochlorobenzene	34·8°	0·2291	5·1	1883	10	757	20·3	20·0 (Y)
Monobrombenzene	34·8°	0·1289	2·0	1888	10	757	8·0	8·0 (Y)
Toluene	34·8°	0·2451	67·6	1014	11	754	46·8	
,, ...	34·8°	0·4672	128·9	1949	11	754	46·7	
Metaxylene (not especially purified) ..	34·8°	0·1080	25·8	1201	17	757	4·17	
,, ,, ,, ..	34·8°	0·1085	25·9	1201	17	758	4·18	
Nitrobenzene	34·8°	0·0090	1·85	1210	23	757	1·16	
,, ...	34·8°	0·0088	1·83	1207	21	757	1·15	
Carbon tetrachloride	34·8°	3·3803	5·55	1913	20	758	169·4	172·6 (R)
,, ,, ...	27·8°	2·4031	3·96	1908	18	756	130·0	130·8 (R)
Chloroform	35·0°	3·0320	64·48	1033	25	755	290·1	301·1 (R)
Ethyl iodide	34·8°	4·2091	683·	1913	20	756	199·0	206·0 (R)
,, ,, ...	27·8°	2·9760	483·	1918	22	756	152·2	154·7 (R)
Carbon bisulphide	20·0°	2·4541	777·4	1206	21	756	296·4	298·1 (R)
Methyl formate..	20·0°	5·1000	195·8	1196	16	756	469·4	
Acetic acid..	35·0°	0·2900	70·0	1960	20	760	26·3	26·5 (R&Y)

Note.—(Y) = Young, *Chem. Soc.*, lv., 486, 1889; (R) = Regnault, *Mèmoires de l'Academie*, xxvi., 239, 1862; (R & Y) = Ramsay and Young, *Chem. Soc.*, xlix., 790, 1886.

approximation to accuracy may be sufficient (see "Comparison of the Vapour-tensions," &c.).

Calculation of Volume of Air passed through a Mixture.—In order to force the air in the measuring vessel through the liquid in the absorption-vessel, it is necessary that it be brought under a pressure equal to that of the atmosphere plus that required to vertically displace the liquid contained in the bulbs, the latter pressure varying with the density and amount of the mixture. The volume of the air under atmospheric pressure may be obtained then as follows:—

Let P represent the pressure of the atmosphere. Let P' represent the pressure which forces the air through the liquid. Let V' represent the volume of air under the pressure P+P'. Let V represent the volume of air under the pressure P.

According to Boyle's law, and inasmuch as the temperature remains constant,—

$$V = \frac{(P + P')\,V'}{P}$$

Calculation of Composition of Mixture of Liquid Vaporised.—As this calculation is simply one of quantitative analysis, it is not necessary to treat of its details.

Calculation of Partial Volumes of Mixtures of Vapours.—Let m represent the quantity of one component in the gaseous mixture. Let M represent its molecular mass. Let 22·32 represent the volume in litres of a grm.-molecule of hydrogen at the temperature 0° and under the pressure 760 m.m. Let a represent the coefficient of expansion. Let v_1 represent the volume of vapour at the temperature of the determination, t, and under the atmospheric pressure, p. We then have—

$$v_1 = 22{\cdot}32\,\frac{m}{M} \times \frac{760\,(1 + a\,t)}{p}.$$

Calculations of Partial Pressures of Components of Vapour Mixture.—Let v_1 represent partial volume of one component. Let v_2 represent partial volume of the other. Let v represent partial volume of air. Let p_1 represent partial pressure of one component. Let p_2 represent partial pressure of the other. Let p represent the atmospheric pressure.

In accordance with Dalton's law,—

$$p_1 = p\,\frac{v_1}{(v + v_1 + v_2)}$$

and—

$$p_2 = p\,\frac{v_2}{(v + v_1 + v_2)}.$$

Comparison of the Vapour-tensions obtained by the Method herein Described and those obtained by other Methods.

Probably the best way to judge of the accuracy of the results obtained in the determination of the vapour-tensions of liquids according to the method described in this paper is to compare them with the results obtained by other investigators working by other methods. Also a criterion of accuracy is to be found in the more or less close concordance of duplicate experiments. In Table I. are given the necessary data of my experiments together with the results obtained by others. It was in some cases necessary to interpolate the results of others inasmuch as my results referred to a limited number of temperatures; the interpolations were made on a large scale, so as to avoid any slight inaccuracy. The original papers of Young and Regnault I am now unable to consult, and have to take their data as given in Landolt and Börnstein's "Physikalische-Chemische Tabellen" or other reproductions.

An inspection of the table shows a most excellent correspondence between my determinations of vapour-tensions and those of others, when the liquid is but slightly volatile, as in the case of the halogen substitution-products of benzene. But when, at the temperature taken for a determination, the elastic force of the vapour exceeds 100 m.m. of mercury, the correspondence becomes less close; and it is at once seen from the data that the greater the volatility of a liquid, the greater the discrepancy. Let us take carbon tetrachloride and ethyl iodide for examples, since determinations of their vapour-tensions were carried out at two different temperatures. For carbon tetrachloride the difference between Regnault's results and mine is $3\frac{2}{10}$ m.m. of mercury at 34·8° and $\frac{8}{10}$ m.m. of mercury at 27·8°; for ethyl iodide, the difference at 34·8° is $7\frac{1}{10}$ m.m. of mercury, and at 27·8° $1\frac{5}{10}$ m.m. of mercury. Other examples point to the same result.

The cause of this want of concordance between my results and those made by other methods has been hinted at in a discussion of the errors to which this method is subject. The assumption, made in the calculations, that the vaporous mixture may be treated as a mixture of ideal gases, cannot be maintained when the volume of the vaporised liquid forms more than a small fraction of the total volume of the gaseous mixture that leaves the absorption vessel. The vapour of ethyl iodide that was carried off by the air, occupied more than a fourth of the total volume, and the other volatile liquids also occupied relatively large volumes; the volumes of the vapours of the less volatile liquids, however, were but a small part of the volume of the air passed through the liquid. And, as has been shown, the less volatile liquids give results perfectly concordant with those obtained by others. Duplicate determinations of the vapour-tensions of some of the liquids, as toluene, nitrobenzene, &c., give almost identical results.

It would not be difficult to apply a correction taking into account the greater volatility of some of the liquids. This I have not, as yet, done, as in certain details I wish to alter the apparatus so as to obtain even more accurate results; thus the use of mercury as the liquid for expelling the air from the measuring vessel would render the system of drying-tubes unnecessary; also, ground-glass joints are undoubtedly preferable to rubber connections. Although it is my intention to study and modify the apparatus further, I do not want to seem to "reserve" this subject of investigation; on the contrary, I would be most glad to see the apparatus tried and tested by others.

Although the results obtained by the employment of this method do not have, in the case of the more volatile liquids, the same degree of accuracy attainable by other methods, still they are suited to the requirements of an investigation of the vapour-tensions of mixtures of liquids, since both liquids, if their vapour-tensions be not too different, are affected alike by any weaknesses in the method. and the phenomenon observed permits of the drawing of theoretic conclusions. Yet I have been careful in the discussion of results to limit myself as much as possible to such as were of the same accuracy as results obtained by others; thus, my method can be counted upon to give results accurate to less than 1 m.m. of mercury when the vapour-tension does not exceed 100 m.m. of mercury, and to less than 2 m.m. of mercury when the vapour-tension is less than 150 m.m. of mercury; as can at once be seen by a comparison of the data due to Young (*loc. cit.*) and Regnault (*loc. cit.*) in the greater number of cases a closer correspondence than to within 2 m.m. cannot be found. However, the conclusions which I draw from my experiments would still hold if the error in the determination were several times greater than that admitted above, inasmuch as it affects each liquid in the same way, so that, while it may affect the absolute accuracy, its relative effect is but slight.

(To be continued).

NOTICES OF BOOKS.

Analytical Chemistry. By N. Menschutkin, Professor in the University of St. Petersburg. Translated from the Third German Edition, under supervision of the Author, by James Locke. London and New York: Macmillan and Co. 1895. 8vo., pp. 512.

In noticing this work we must distinguish between the matter and the language. The author's instructions will be pronounced excellent by all competent chemists who may give them the necessary examination. We do not indeed, see that the author proposes any novel reaction or brings forward any new general method. But he lays due weight on the acquisition of the habit of *chemical thought*, which he justly pronounces the most important object of practical work. Mere mechanical study he appraises at a very low value, considering that it cannot in a single instance teach how to make a correct analysis, to say nothing about developing the faculty of chemical thought. He condemns the practice of allowing the student to enter upon analysis before he has been prepared by a thorough training in general chemistry. He insists that the necessary knowledge should be estimated not by the number of single and isolated facts with which he is familiar, but by the clearness with which he understands fundamental chemical phenomena and theories,—points not always duly appreciated by the routine examiner.

The work consists of two main parts, a qualitative and a quantitative. The author holds that the student should in the outset devote himself to the former branch alone.

In a supplement to the section on qualitative analysis the author explains the use of the blowpipe,—which he remarks has almost completely disappeared from the laboratory with the introduction of the Bunsen gas-burner, though for the prospector and the traveller it retains all its former value,—of Bunsen's flame-reactions, which are here very fully expounded, and of spectrum analysis, which receives here an attention unusual in analytical manuals.

Prof. Menschutkin describes the spectroscope of Bunsen and Kirchoff (not Kirschoff!), the reversal of the spectrum, the dependence of the spectrum upon the conditions of the experiment, the flame spectra, the spark spectra, the phosphorescence spectra, and absorption spectra.

The recent results of Crookes, and of Krüss and Nilson, are mentioned, but with the remark that the subject has not yet obtained the wide attention which it requires and merits.

In the quantitative part of the work electrolytic determinations are mentioned somewhat briefly, with a recommendation of thermo-batteries, or of Meidinger and Bunsen elements. We find no reference to gas analysis, which is now of growing importance.

The subject-matter of this work is of unquestionable value, but the language employed is not incapable of amendment. Thus we find the term "metalloids" constantly used. The element which we commonly, in virtue of priority, name "glucinium," is here termed "beryllium," and selenium and tellurium are made to rank as metals. In the very first sentence of the book we read:—"the analytical branch of the science *is given* a sharply-defined position." "Is given" and kindred expressions have come to be tolerated in newspaper paragraphs, but they are painful in a scientific treatise.

Continuity of the Colligative Properties and the Polymerisation of Matter through its Three Conditions. By Julien Delaite. Brussels: F. Hayez. 1895.

The author formulates the following law:—

"The density of a mixture of several solutions, having no chemical action upon each other, is, if the temperature remains constant, the sum of the densities of the component solutions, if we refer their density to the total volume and accept as true the law of Boyle-Mariotte applied to the dissolved salt."

He gives a table of all the atomic volumes, showing that the condensation is inversely as the chemical activity of the elements. Potassium, sodium, calcium, bromine, all very active substances, have low atomic coefficients, whilst the heavy metals and carbon are most strongly condensed. Diamond is said to have the strongest condensation, = 3271.

Another table gives the "integral weights" of the elements, not at all coincident with their atomic weights, and ranging from $H = 1$ to $Os = 2498^{28}$. Helium and argon do not appear to have come under the author's investigation. By combining the atomic coefficients and the integral weights, Dr. Delaite arranges tbe elements in eight series. He remarks that though carbon possesses the highest atomic coefficient, yet its integral weight is relatively low, which partly explains the great activity of this substance in organic compounds. He believes that the chemistry yet to be constituted will be better entitled than that of Sterry Hunt to the title of a "New Chemical System."

A New Bactericide.—German medical and hygienic papers are now discussing a new bactericide bearing the utterly misleading name of "argonine." We hasten to inform our readers that this novelty is not a compound or derivative of argon, with which it has not the remotest connection. It is a compound of silver and caseine.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 13, September 23, 1895.

Specimen of Black Carbon from Brazil.—Henri Moissan.—This carbon is a variety of black diamond which sometimes exhibits a confused crystallisation, and sometimes presents a shagreeny aspect. M. des Cloizeau in his study on carbon has mentioned various crystals, among which is a complete cube with rounded edges. Such carbon is met chiefly in the province of Bahia and in small quantities in Borneo. It is much valued for tipping the crowns of boring apparatus. When of good quality its value is about 65 francs per carat. The sample which I have the honour of submitting to the Academy was found in the region between the Rio à Rancador and the brook das Bicas in the territory of the town of Lençoes. It weighs 630 grms. = 3073 carats, and is consequently the largest specimen which has been hitherto found. It is of a rounded form, distinctly black. On examination with a low microscopic power it has the appearance of a substance from which gases have escaped whilst in a pasty state. It is porous, and has lost about 19 grms. in weight since being taken out of the earth. The Brazilian miners have to pay to the owners of the lands on which they work a royalty of 25 per cent on the gross yield of stones and also a tax to the Government.

Composition of Pelageine.—Dr. A. B. Griffiths and C. Platt.—The authors have determined the chemical composition of the violet pigment of the Medusa (*Pelagia*). The pigment and fatty substances are soluble in boiling alcohol and ether. The filtered solution is evaporated to dryness; the residue is treated with a solution of soda, and the pigment rapidly extracted with carbon disulphide. On spontaneous evaporation the violet pigment is left as an amorphous residue. Of this pigment 0·2058 grm. yielded 0·47325 c.c. (?) of carbonic acid and 0·081 of water. 0·4605 of the pigment yield 15·15 c.c. of nitrogen at the barometric pressure of 742 m.m. and the temperature of 15°. The results answer to the formula $C_{20}H_{17}NO_7$. This pigment, which we name pelageine, is soluble in alcohol, ether, and acetic acid, insoluble in water, and very soluble in carbon disulphide. In an isolated state pelageine is bleached by light, and on spectroscopic examination it does not show any characteristic absorption-bands.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 9, 1895.

Thermic Study of the Anhydrous Barium and Strontium Iodides.—M. Tassily.

Researches on the Combining-heats of Mercury with (other) Elements.—Raoul Varet.—A determination of combining-heat of mercury with iodine (= +24·7 cal.), bromine (= +40·7 cal.), oxygen (= +21·3 cal.), and chlorine (= +49·8 cal.).

Amorphous State of Melted Bodies.—C. Tanret.—Not all crystalline bodies re-crystallise on becoming solid after fusion. Some remain amorphous; and many, which crystallise under ordinary conditions, become amorphous if cooled abruptly. Among those which are thus rendered amorphous after fusion, the author mentions the pentacetines of glucose and the hexacetines of the active inosites.

Contribution to the Study of the Dissociation of Active Salts in Solution.—Ph. A. Guye and B. Rossi.—This voluminous paper is not adapted for useful abstraction, and does not merit insertion *in extenso*.

Calcium Phosphate in Milk.—L. Vaudin.

Isomeric States of Mercury Oxide.—Raoul Varet.

Volumetric Determination of Zinc.—L. Barthe.—A reply to the criticisms of H. Lescœur, who has operated upon a sample containing 13·9 per cent of impurities.

Preparation of Ethylamine by the Reduction of Ammonium Aldehydate.—Ferdinand Jean.—The author puts in a flask 10 grms. ammonium aldehydate, recently prepared, along with a little water and 20 grms. zinc powder. He then adds, in ten minutes, 150 grms. of hydrochloric acid (1 : 2), and after ten more minutes, 20 grms. concentrated hydrochloric acid, moderating the reaction by cooling the flask in a current of water. After forty-five minutes, it is heated for half an hour on the water bath. To obtain the ethylamine a large excess of soda is added so as to dissolve the zinc salt, and a violent current of steam is passed into the flask whilst heat is still applied.

Action of the Primary Aromatic Amines on the Non-symmetric Ketonic Compounds.—L. Simon.—This memoir is not adapted for useful abstraction.

Dimethylamido-α-caproïc Acid.—E. Dunvillier.—Also not adapted for abstraction.

Propionic Ethylhydantoine (Ethyluraminodopropane).—E. Dunvillier.—Ethylamidopropionic acid yielding merely a hydantoine and not the corresponding hydantoic acid, and the amidic acids of the amines of the fatty series yielding merely a creatinine and rarely a creatine, the author is led to believe that the same amido-acids generally yield merely hydantoines.

Three Octochlorophenols.—Et. Barral.—These octochlorophenols possess certain identical properties which are also common to hexachlorophenol:—(1) Reduction to pentachlorophenol by tin and hydrochloric acid; (2) decomposition by heat into chlorine and products containing perchlorodioxyphenylene; (3) formation of pentachlorophenol acetate with acetic anhydride. These isomeric octochlorophenols are much more stable than hexachlorophenol. They are perchloro-acetones, differing from hexachlorophenol by Cl_2; that is, *trichlorides of pentachloro-cyclo-hexa-diene-one* in which the position of the three atoms of chlorine has yet to be determined.

Hexamethyleneamine. Action of Phenylhydrazin Hydrochlorate.—M. Delepine.—Here we have the total elimination of the typical hydrogen. Methylenephenylhydrazin, $CH_2CH_2{=}N{-}NH{-}C_6H_5$, which would correspond to the general formula of the phenylhydrazin aldehyds, still reacts upon formic aldehyd to yield trimethylene-diphenyldihydrazin.

Hexamethyleneamine Chloromercurates and Iodomercurate.—M. Delepine.—The author has obtained three chloromercurates and one iodomercurate, and considers it certain that by varying the conditions we may augment their number on account of the multiplicity of basic functions in the molecule.

Novel Reactions of Morphia.—G. Bruylants.—Already inserted.

Untrustworthiness of Cremometers for Determining the Fatty Matter in Pasteurised Milk.—P. Cazeneuve and E. Haddon.

Sterilisation of Milk, and on Lactic Fermentation. P. Cazeneuve.—The author's conclusions are:—1. If it is true that a heat of 110° (Pasteur, Hueppe) for half an hour is required to kill the lactic ferment, a temperature of 98° to 100° applied for an hour often destroys it, and in all cases attenuates it so far as to render it sterile in deoxygenated milk. As for the pathogenic ferments they are certainly destroyed. 2. In industry the apparatus which I have described permitting the complete immersion in boiling water of the sterilising bottles and the total deoxygenation of the milk and the containing vessel secures its indefinite preservation without any savour of rancidity and without coagulation. 3. Milk at 98—100° has digestive properties, as demonstrated by clinical observation and experiment (Dr. Rodot), at least equal to those of raw milk, whilst it has the well known superiority of not being the vehicle of certain contagious microbia (Dr. Budin, &c.). It has the advantage over milk boiled at 110—120° of not turning yellow, and not taking a taste of burning or of peptone so frequently met with in milks sterilised at this temperature. 4. My observations have permitted me to establish that the lactic ferment appears little diffused in the air. Milk is chiefly contaminated by contact with impure objects.

Mordant of Glucina.—Maurice Prudhomme.—In preparing the mordant the author sets out with a crystalline glucinium sulphate, free from iron, and containing merely traces of alumina. 10 grms. of this sulphate were dissolved in 75 c.c. of distilled water, precipitated with ammonia, and pure ammonium carbonate is added to the solution. After twenty-four hours, it is filtered and heated in the water-bath to expel any excess of ammonium carbonate. The deposit of glucinium carbonate is redissolved in acetic acid and the mordant is made up to 100 c.c. The cloth worked in this bath is dried in the stove, aged for twenty-four hours in a moist atmosphere at about 35°, and dunged in a dilute solution of ammonia at 60°. The swatches took a garnet shade corresponding to *violet-red* 1, 4/10 black of Chevreul's chromatic circle. The author concludes that glucina behaves as a protoxide and not as a sesquioxide from a tinctorial point of view.

MISCELLANEOUS.

Impurities in Milk.—The *Medical Press* of October 2nd quotes Dr. Buckhaus, of Berlin, that this city consumes in its milk-supply 3 cwts. of cow-dung. Whether this is the daily consumption of so unsavoury an addition we do not learn.

Diamonds.—According to the *Chemiker Zeitung* a diamondiferous rock has been discovered on the River Kamanka, in the Southern Ural. The diamonds are said to resemble those of Brazil, having a purer water than those of South Africa.

Discovery of Saltpetre at the Cape. — Attention has been called from time to time to the importance of searching for deposits of potassium salts in the Colonies and India. According to *South Africa* it appears that beds of earth rich in potassium nitrate have been discovered in the Cape Colony, and are now being worked on a practical scale. Samples have been found containing as much as 70 per cent of this valuable salt, but the average seems to range from 12 to 15 per cent. Of course the extent of the deposits has not yet been determined. The value of this discovery, if the supply is considerable, is beyond question.

Influence of the Presence of Lead Acetates on the Results of the Determination of Inverted Sugar by the Fehling-Soxhlet Method.—Arthur Bornträger.—The author confirms the statement of C. H. Gill, which appeared in a paper on the examination of glucose-containing sugars, read before the Chemical Society, March 16, 1871. Gill arrived at the conclusion that in presence of basic lead acetate, solutions of invert sugar seem to have a less reductive power than in the absence of the lead salt. Borntrager expresses his regret that he did not meet with Gill's original paper, but only imperfect, and to some extent misleading abstracts.—*Deutsche Zucker-Industrie*, August 9, 1895.

Errata.—The title of the paper by Messrs. Auden and Fowler (p. 163) should read "The Action of Nitric *Oxide* on Certain Salts," instead of "Nitric *Acid*." P. 124, Queen's College, Cork, *for* "Assistant--D. J. O'Mahony, F.C.S.," *read* "Demonstrator—R. E. Doran, F.C.S."

THE CHEMICAL NEWS.

Vol. LXXII., No. 1873.

ON THE SENSITISING ACTION OF DYES ON GELATINOBROMIDE PLATES.*

(Abstract).

By C. H. BOTHAMLEY, F.I.C., F.C.S.

Although many dyes have been examined since H. W. Vogel's discovery in 1873, very few of them exert any marked effect in making gelatinobromide plates sensitive to the less refrangible rays of the spectrum. Only cyanin and the dyes of the eosin group (including the rhodamines), with perhaps malachite-green, alizarin-blue, and chrysoidine, exert any practically useful effect.

The main points established by previous observers may be summarised as follows:—(1) all the dyes that act as sensitisers are readily affected by light when in contact with paper, fabrics, &c.; (2) in order that a dye may act as a sensitiser it must have the power of entering into intimate union with silver bromide, forming a kind of lake; and (3) it must show a strong absorption-band for the particular rays for which it is to sensitise. It is important to observe that the converse of these statements is not necessarily true, since several dyes that have all these properties show no appreciable sensitising action.

Experiments by Dr. E. Vogel on the rate of fading and the sensitising action of the eosin dyes, led him to the conclusion that the order of sensitising effect coincides with the order of fading when the dyes are exposed to light. The order in which he places the dyes does not, however, correspond with the order of fading as observed in dyed fabrics, and the experimental method that he used is open to criticism.

The author's observations on the fading of the various sensitisers when exposed to light in contact with gelatin alone, led him to the conclusion that, although all the sensitisers are readily affected by light, the order of sensitising effect does not necessarily correspond with the order of fading, whether the dyes belong to the same chemical group or not.

There are two chief hypotheses as to the mode in which the dyes act, namely, (1), the view held by Abney, that the dye itself is oxidised by the action of light, the oxidation product remaining in contact with the silver bromide; and when the plate is treated with the developer, the latter and the oxidation product, acting simultaneously on the silver bromide, bring about its reduction; and (2), the view first definitely formulated by Eder and endorsed by Vogel, namely, that the energy absorbed by the dyed silver bromide is partially used up in bringing about the chemical decomposition of the silver bromide, instead of being almost entirely converted into heat as when absorbed by the dye alone.

The author has found that the less refrangible rays will produce a photographic image on the sensitised gelatinobromide plates when they are immersed in powerful reducing solutions, such as a mixture of sodium sulphite and pyrogallol. This holds good for cyanin, the eosin dyes, the rhodamines, and quinoline-red, whether the sensitiser has been added to the emulsion or has been applied to the plate in the form of a bath. It is therefore impossible to attribute the sensitising effect to any intermediate oxidation of the dye.

Experiments with various reagents, such as potassium bromide, potassium dichromate, mercuric chloride, and dilute hydrogen peroxide, seem to show that the chemical nature of the latent image produced by the less refrangible rays on the specially sensitised plates, is precisely the same as that of the latent image produced by the more refrangible rays in the ordinary way.

Further proof in the same direction is afforded by the fact that the effect of the sensitisers extends to the production of a visible effect by the prolonged action of light.

The balance of evidence is therefore greatly in favour of the view that the dye absorbs the particular groups of rays, and, in some way which is not at all clear, hands on the energy to the silver bromide with which it is intimately associated, and which is thereby decomposed.

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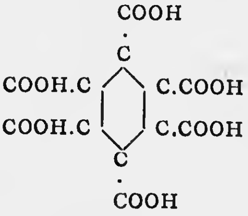
* Read before the British Association (Section B), Ipswich Meeting, 1895.

NOTE ON THE

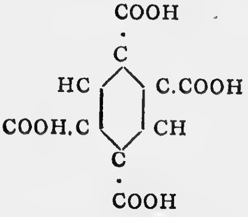
CONSTITUTION OF CAMPHORIC ACID.*

By J. J. SUDBOROUGH, D.Sc., Ph.D., F.I.C.,
Lecturer on Organic Chemistry, University College, Nottingham.

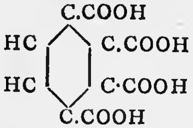
The behaviour of camphoric acid on esterification (J. W. Brühl, *Ber.*, 1893, xxvi., 284) is very similar to that of some of the aromatic polycarboxylic acids investigated by V. Meyer and Sudborough (*Ber.*, 1894, xxvii., 3146). These authors have shown that a carboxylic group which has substituting groups in the two ortho-positions is incapable of yielding an ester under the usual treatment with alcohol and hydrogen chloride. Thus, mellitic acid—



gives no ester. Pyromellitic acid—

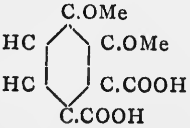


gives a neutral ester, $C_6H_2(COOEt)_4$. And prehnitic acid—



gives a dialkylic ester, $C_6H_2(COOH)_2(COOEt)_2$.

Wegscheider (*Monatsheft.*, 1895, xvi., 75) has since shown that hemipinic acid—



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* Read before the British Association (Section B), Ipswich Meeting 1895.

which is a dicarboxylic acid, yields a mono-alkylic ester, and thus resembles camphoric acid very closely indeed.

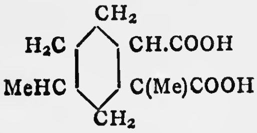
It is true of both hemipinic and camphoric acid that if the esterification is carried out for some time at the boiling-point of the alcohol, small quantities of the neutral esters are also formed; the main product, however, is always a mono-alkylic ester.

The reason for such behaviour is, beyond doubt, to be sought for in the stereo-chemistry of the molecule, the ortho-substituting groups hindering the action of the reagent which is employed.

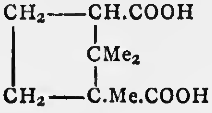
This view has received support from the recent investigations of V. Meyer on the esterification of many other aromatic acids, and also from those of the author on substituted benzoyl chlorides and benzamides (*Journ. Chem. Soc.*, 1895, 587 and 601). Whether we regard the substituting groups as filling up the space and thus preventing the formation of some intermediate additive compound, as Wegscheider suggests, or whether we regard them as simply preventing the entrance of the alkylic groups into the molecule, is of no importance in the present discussion.

We are thus, to some extent, justified in concluding that the characteristic behaviour of camphoric acid on esterification is due to stereo-chemical causes. Any constitutional formula proposed for the acid should therefore indicate stereo-chemical grounds for such behaviour.

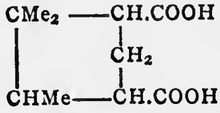
If we take three of the formulæ which have been more or less generally accepted, viz.—



Armstrong.



Bredt.



Tiemann.

we find that in no case have we a carboxylic group which has substituting groups in the two ortho-positions. In the formulæ of Armstrong and of Bredt, however, one carboxyl is ortho-substituted on the one side, and then has a methyl group attached to the same carbon atom to which it is united. It may be that this methyl group has a similar influence from a stereo-chemical point of view as a methyl group in the ortho position. If this is really so, then we can see sufficient grounds for the analogy between camphoric acid and hemipinic acid. If, however, we take the formula recently suggested by Tiemann (*Ber.*, 1895, xxviii., 1079) we see that both carboxylic groups are similarly situated; they both have substituting groups in one ortho position, but not in the other; and, further, neither has a substituting group attached to the same carbon atom to which it is united. We thus see no reason why one carboxyl should behave differently from the other on esterification. It must be pointed out that hemipinic, mellitic, and the other acids are all benzene derivatives, whereas camphoric acid, according to Armstrong, is a hexamethylene derivative, and according to Bredt and to Tiemann a pentamethylene derivative. J. van Loon has recently shown (*Ber.*, 1895, xxviii., 1270) that polycarbacids of the hexamethylene series, *e.g.*, hydromellitic and isohydromellitic acid, behave very similarly to the acids of the benzene series, except for the difference that is caused by cis- and trans-isomerism.

ON SOME STILBENE DERIVATIVES.*

By J. J. SUDBOROUGH, D.Sc., Ph.D., F.I C.

The author has prepared monochloro-, methyl-chloro-, and ethyl-chloro-stilbene by the action of phosphorus pentachloride on deoxybenzoïn and on its methyl and ethyl derivatives. The monochloro-stilbene differs from that described by Zinin (*Annalen*, cxlix., 375), as it is a solid, which crystallises from alcohol in large colourless plates. It melts at 53°—54°, and yields additive compounds with bromine, with chlorine, and with "nitrous acid." These, together with the corresponding compounds obtained from methyl- and from ethyl-chloro-stilbene, are described. An oily monochloro-stilbene, corresponding to that of Zinin, has also been prepared, and is being subjected to further examination in order to determine whether it is merely an impure form of the crystalline compound or a true stereo-isomeride.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 179).

To have the air motionless, at the same time, outside and inside a closed room, however large, is a condition so rare that almost all spectroscopists acknowledge that the sodium D line is *always* seen in a Bunsen burner or in a blowpipe fed with hydrogen.

When one has a chance of having the air relatively pure, the disturbance which one is obliged to make one's self in the room in order to work soon sullies the purity of the medium.

I have ascertained that the time suitable for the experiments themselves is very small; it is at the most an hour and a half a day; and it is only in the morning, from 9 to 11 o'clock, when the external air has been saturated with moisture for several days, that we can hope to find it at Brussels, on condition of having taken care to wash, with plenty of water, the floor and the walls of the room the previous evening, in order to rid one's self, so far as may be, from dust accumulations, of having admitted thither air saturated with moisture, of keeping the floor wet, of refraining from walking about the room, and of only being helped by a single assistant or a single witness. When the floor is dry and the air of the room is disturbed by walking about, or by draughts caused by the doors, by the window-shutters, and above all by the roof of the room, the pure deep blue colour characteristic of the flame of a Bunsen burner alters towards indigo, to become finally a distinct violet, and even reddish; one then often observes in it bright points which give a yellow light.

The prismatic analysis of the flame shows in it the existence of sodium and calcium in an intermittent or continuous manner, according to the magnitude of the disturbance of the air. The introduction of hydrochloric acid in this flame allows one to see the spectrum of calcium with great relative clearness.

In air disturbed by motion, the invisible flame of pure hydrogen, the blowpipe flame of hydrocarbon in air, or of oxyhydrogen, turns distinctly yellow, often even red, and becomes very bright. The colour and brightness of this flame increases with the magnitude of the disturbance.

The difficulties against which one has to strive whilst one is attempting to ascertain the truth of facts, do not include simply such impurities as the ordinary air may contain, but depend equally on the state of purity of the gases employed and of the apparatus through which one

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* Read before the British Association (Section B), Ipswich Meeting, 1895.

passes them, or on the burner in which one completes the combustion of them.

It is essential that the illuminating gas, hydrogen, air, and oxygen which feed the blowpipes should themselves be entirely freed from suspended particles of sodium or calcium.

I have found that one of the best and surest methods of purifying illuminating gas, hydrogen, oxygen, and air from all suspended particles, is to let them pass through pure boiling water, and to pass them into and store them for at least twenty-four hours undisturbed in large gasometers, over water free from volatile bodies and made alkaline by lime or baryta.

When afterwards used they do not show any trace of the spectrum of sodium or calcium.

It is so difficult to deprive dry air in motion of suspended matter, that one distinctly notices the presence of sodium in the flame of a platinum or silver blowpipe when fed with hydrogen or purified illuminating gas, and either external or internal air supplied and purified by its passage through water-bellows or a water-pump. I have only succeeded in removing the sodium which is contained in insoluble suspended particles from the external or internal atmosphere, even with the assistance of a water-pump, by passing it through a metal heater containing pure boiling water.

Having regulated the supply of purified air and the boiling of the water, so as to obtain a supply of air and water vapour in nearly equal volumes, the condensation of steam, during its passage along a condenser of well-polished tin, ensures the deposit of such insoluble particles as may have survived the purification by the pump, and thus gives, when using either illuminating gas or pure hydrogen, a blowpipe flame in which spectrum analysis does not enable one to detect the sodium line, it being well understood that the *air of the room or of a lofty and comparatively confined closet*, with damp walls, in which one is working, is itself entirely freed from sodium particles.

The steam, when condensing, deposits with itself the insoluble matter suspended in the air supplied by the bellows or the pump.

I have tried an experiment, on s very large scale, for the purpose of ascertaining the weight of sodium particles thus eliminated. I worked during a moderate southerly breeze, on air taken from the street in which I live, running from east to west, 9 metres above the ground, which is about 50 metres above the surface of the river running through the town, and about 67 metres above sea-level. Whilst the apparatus was working I took pains to satisfy myself, by several repetitions, that after the condensation of steam the air mixed with it was completely free from sodium particles.

The condensed water, as it was formed, was passed through a double filter-paper that had been freed by a simple process from all traces of mineral matter, and held in a covered platinum funnel. I found that the combustion, in a closed vessel and at the lowest possible temperature, of the double filter, through which had passed *ten litres* of water after the pump had been working for sixteen hours, only left 0·00023 grm. of brown ferruginous ash,—that is to say, 23/10,000,000 of its weight, supposing, be it understood, that not a particle* of suspended matter had been retained in the well-polished tin condenser. The volume of air supplied by the pump to the distilling apparatus amounted to about 17 cubic metres.

In whatever manner the water was collected into a glass jar, it was impossible for me to detect in it, by spectrum analysis, the slightest sign of the sodium line. The water-pump, therefore, had robbed the air of its *soluble compounds of sodium;* on the other hand, the brownish ash, having been moistened with hydrochloric acid freshly prepared in the platinum dish, and introduced into an hydrogen flame on the end of a platinum loop, at once coloured it a *brilliant yellow*, and with the spectroscope I recognised the presence of *calcium* and *sodium*.

The last remaining cause of the difficulties which one meets in spectrum analysis, when one attempts to solve important questions, rests in the apparatus used for producing the flames.

As regards platinum, experience has taught me that by melting and refining one rids it entirely of sodium. As a matter of fact I have never succeeded in detecting the appearance of the sodium line in platinum which has been purified by re-melting in the air in an oxyhydrogen blowpipe. I have noticed, on several occasions, that platinum which had been melted in a lime crucible, on being re-melted in an oxyhydrogen flame, gave temporarily a calcium spectrum. Whatever the reason might be, when made into either sheet or wire, the re-melting in air got rid of the calcium.

If platinum which has been kept for some time in air, *even protected from dust*, be put into the flame of a Bunsen burner or an hydrogen flame, it at once colours them yellow and shows the sodium line, but never a calcium spectrum, not even when moistened with hydrochloric acid. The fact that these flames turn yellow, first noticed by Messrs. Bunsen and Kirchhoff, is known by all spectroscopists. *This colour disappears when the metal is raised to a white heat.*

If platinum which has been lying in air, either *in a room* or *outside*, and unprotected from the dust, be put into the flame of a Bunsen burner or an hydrogen flame, it colours them yellow tinged with red: this colour lasts so long as the platinum has not been melted and refined in a lime crucible, or even if it has not been treated when warm with a mixture of hydrofluoric and hydrochloric acids diluted with their own weight of water. I have ascertained that the particles suspended in the air, both in the room and outside in the town of Brussels, which are insoluble in water, include, besides organic salts, silicates of alumina, calcium, iron, and sodium, carbonate of calcium, and silica. I have looked for potassium without being able to find it.

Experience has taught me that the tubes and fittings of platinum intended to be used in accurate spectroscopic researches ought to be kept protected from atmospheric dust, and before making use of them it is essential to give them a cleaning with dilute hydrofluoric and hydrochloric acids, and then with distilled water. I have ascertained as a fact that it is in the form of a fused silicate that the sodium remains on the surface of dusty platinum which has been raised to a white heat.

I have mentioned above that pure platinum, if kept some time in air and *protected from dust*, colours the flame of a Bunsen burner yellow, and gives the sodium line.

I tried some experiments to make sure of this fact, and found that *pure* platinum—either wire, sheet, or spongy—can be kept a great length of time in the damp open air, as well as in an air current issuing from a gasometer where it has been stored over water for twenty-four hours, and whence it issues saturated with water-vapour, without acquiring the power of colouring an hydrogen flame yellow, or giving the slightest trace of the sodium line.

It is the same with air purified by passing it through a metal boiler filled with boiling water, as I have explained above. This air is so completely free from sodium that not only can one leave platinum in it without contaminating it with sodium, but one can pass a spark from a powerful induction-coil through it, between platinum points or points of platinum covered with iridium free from soda, and still a spectrum analysis of the spark does not show the sodium lines among the atmospheric lines (*see* Note). This image can always be seen in the spark made in *so-called pure air, even when hydrogen and illuminating gas can be burnt in it without showing the presence of sodium in the spectroscope.* When describing

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* A filter of good paper, treated successively with hydrochloric and hydrofluoric acids, left no trace of ash when burnt.

the spectroscopic study of lithium I shall return to this last fact.

(Note.—I made this experiment in an apparatus the details of which are known. It consisted, shortly. of a tube of hard colourless glass, 12 c.m. long, 8 c.m. internal diameter, and 10 c.m. external diameter.

A disc of hard glass, ground and polished on one side, 2 c.m. thick and 10 c.m. diameter, was fixed on either open end of the tube by means of clamps held together by metal rods with screwed ends. Each disc was pierced in the middle with a slightly conical hole, about 1 c.m. diameter, into which was carefully fitted a plug of pure silver, terminating outside in a small ring, meant for making contact either with the coil or the condenser. In the end of the conical silver plugs which pierced the discs was drilled a deep cylindrical hole 1½ m.m. in diameter, and tapped, for screwing in one of the ends of a platinum rod of the same diameter, whose end was also screwed. To the other end of the platinum rod was attached a ball of the same metal, 3 m.m. in diameter, or a ball of platinum coated with pure iridium which had been fused on with the oxy-coal-gas blowpipe.

The distance between the platinum balls is adjusted by screwing the ends of the platinum rods more or less deeply into the screw holes in the silver plugs, which are kept in the discs by frictional grip. After some trials I varied this distance between 5 and 10 m.m.

In the middle of the space between the hole pierced in each disc and the inner surface of the tube is drilled a second hole, 6 m.m. in diameter, into which is fitted, by grinding with emery, a hard glass tap, so as to provide each disc with a tap for letting the air to be submitted to the electric discharge into the tube.

With the exception of the silver plugs and their extensions, the platinum rods and balls used as electrodes, the apparatus was made of hard glass, of which all the parts in mutual contact were ground and polished with emery, and kept pressed one against the other in such a manner as to form an air-tight chamber, and preserve by atmospheric pressure the air which was contained in it.

In order to rid the apparatus of all traces of free sodium compounds I made the following arrangements. After having washed the apparatus, short of its silver plugs, several times with pure water, I put it, whilst it was still wet, by means of the taps fitted to it, in communication with the gasometer containing the air which I wished to examine, and passed a rapid current of this air through it. I then adjusted the silver plugs and their extensions, the platinum rods and balls, which had just been washed, first with dilute hydrofluoric acid and then with pure water, which had been distilled and condensed into the platinum funnel.

The balls of pure platinum, or of platinum coated with pure iridium, having been first set to the required interval, and the apparatus having been fixed vertically in front of, and as near as possible to, the slit of the spectroscope, I passed alternately sparks and a brush discharge between the balls, whilst a current of the air under examination passed through the apparatus.

This current of air was supplied:—

1. By a gasometer in which the external air, washed simply by the pump, had remained for twenty-four hours over water made alkaline by baryta.
2. By a gasometer in which was received direct the air delivered by a water-pump into boiling water contained in a copper boiler surmounted by a chamber communicating with a tin refrigerator, which was kept at a low temperature by ice constantly renewed in order to condense the steam mixed with an almost equal volume of air from the pump.

When working in this manner, I observed that spectrum analysis, whether of the spark or brush discharge, however powerful they were, showed a spectrum *without* the double D line. With the spark long or short I observed only the spectrum of atmospheric lines, and with the *strong* spark the spectrum of these latter lines, near to which appeared some *bright* lines, due either to platinum or iridium, according to the material of the surface of the balls used.

For this purpose I used in succession M. Hilger's direct-vision spectroscope, Steinheil's spectroscope, and lastly, M. Duboscq's large spectroscope with three prisms.

The absence of the yellow sodium line in the spectrum of the electric current passing through air saturated with moisture and purified by the methods described above, surprised the spectroscopists to whom I told my results. I will say in support of the perfect accuracy of this research, that during the revision of my spectroscopic studies with M. Depaire, we both decided, after several trials, that we could not see the yellow sodium line in the spectrum of a discharge passed through the partially saturated air in his spectroscopic laboratory.

Trying one day if we could obtain a compound of magnesium sufficiently free from sodium as not to show the sodium line on spectrum analysis of the spark through it, we not only ascertained the possibility of attaining this entire freedom, but we found also that the surrounding air, which fed the tube on which we were engaged, was free of sodium.

With the hope of being able to learn something of the nature of the substance which occasionally gave to the hydrogen made by water electrolysis, or by the decomposition of zinc or of zinc and lead by dilute sulphuric acid, the property of burning with a *ruddy yellow* flame, I filled the apparatus described above with hydrogen having this property, and whilst the current was passing through it I made a spectroscopic examination of the spark, weak or strong, passed through it.

I noticed that near the sodium line and the C and F hydrogen lines, the spectrum showed some faint lines, both red and distinctly green, grouped like nitrogen lines, and whose position coincided with that of nitrogen lines.

The presence of nitrogen is accounted for, since the hydrogen was collected and stored over aërated water.

Having replaced the gas with hydrogen deprived of the power of burning with a slightly visible flame, I proved by a spectroscopic examination of the spark through this gas the absence of the sodium line in the spectrum; but the presence, fully as noticeable, of the faint red and green lines seen in the gas endued with the property of burning with a visible flame.

The nature of the substance which, in certain conditions, gives hydrogen the property of burning with a ruddy flame remains to be discovered).

(To be continued).

CITRIC AND TARTARIC ACIDS FROM CANE-SUGAR.

(Third Note).

By Dr. T. L. PHIPSON.

Although I have not finished my investigations on this subject, I hasten to reply to those chemists who have not succeeded in obtaining the results alluded to in my former notes. It is easy to point out where their error lies, but it will perhaps not be so easy to get them to acknowledge it. They have failed to obtain the products by oxidation because they have not employed a sufficient quantity of permanganic acid. If they had jotted down the proportions requisite to supply the needful quantity of oxygen in order to convert cane-sugar to citric acid, they would have found that it requires at least as much permanganate as the weight of sugar employed. No lime precipitates of organic acids are obtained with small quantities, and hence the errors of observation alluded to.

These gentlemen all assert that the precipitate on boiling consists of sulphate of lime with no trace of organic acid, and that when nitric acid is used instead of sulphuric acid to acidify the sugar solution, no precipitate is obtained.

Here is an experiment made without sulphuric acid, in which nitric acid alone was used:—

Equal weights of sugar, nitric acid, and permanganate of potash are taken, and the mixed solution is left for twenty-four hours in the cold. The clear solution is neutralised by carbonate of lime, which occasions a copious precipitate. The clear liquid from this precipitate, when boiled, yields a further smaller precipitate. The first contains tartaric acid, and perhaps saccharic acid, which has the same composition as citric acid. It is soluble without effervescence in acetic acid, and therefore contains no oxalic acid nor carbonic acid. The second precipitate is citrate of lime.

If the clear liquid, instead of being neutralised by carbonate of lime, is almost neutralised by carbonate of potash, and stirred with a glass rod whilst still acid, bitartrate of potash is precipitated. The liquid filtered from the lime salts contains the whole of the manganese.

The Casa Mia Laboratory, Putney,
October 10, 1895.

THE SEPARATION OF ARSENIC FROM OTHER ELEMENTS BY MEANS OF METHYLIC ALCOHOL AND HYDROCHLORIC ACID.

By CARL FRIEDHEIM and PAUL MICHAELIS.

The method proposed by Schneider and almost simultaneously by Fyfe, subsequently repeatedly tested and modified,—*i. e.*, to separate arsenic from other elements in the state of a volatile trichloride, by means of hydrochloric acid or sodium chloride and sulphuric acid,—has been re-modelled in a much more useful and generally applicable state by E. Fischer, who effects the distillation in certain conditions after the addition of ferrous chloride and hydrochloric acid. Hufschmidt, as also Classen and Ludwig, expedite the elimination of the arsenic in an extraordinary degree by the introduction of gaseous hydrochloric acid.

If this method is used for separating arsenic from other metals precipitable in an acid solution by means of sulphuretted hydrogen, the presence of ferric chloride at most presents the disadvantage that sulphur is carried down along with the sulphides. But if nickel, cobalt, and other elements of the ammonium sulphide group are present, their determination in the same specimen becomes very difficult, and that of iron impossible.

Also in the separation of arsenic from tungsten, vanadium, and molybdenum, in company with which it is found in numerous so-called complex combinations, the above-mentioned method would be as good as inapplicable. Tungsten would be in part separated out during the distillation, and have a disturbing influence. On the other hand, in consequence of the presence of the great quantity of ferrous chloride, it could scarcely be precipitated by concentration. The determination of vanadium by precipitation with mercurous nitrate would be rendered difficult by the simultaneous precipitation of mercurous chloride, and molybdenum could be separated from iron only by means of ammonium sulphide, which is neither accurate nor convenient.

In nearly all these and in numerous other cases we have found it preferable to substitute for ferrous chloride, methylic alcohol, because after distillation it leaves behind no fire-proof substance, but at most some carbon which is easily filtered or burnt off.

I. *Behaviour of Arsenic Acid with Methylic Alcohol and Gaseous Hydrochloric Acid. Modus operandi.*

Arsenic acid, on treatment with methylic alcohol and hydrochloric acid, is not esterified as such, but reduced to arsen-trioxide, which then seems to evaporate in the form of its ester, a view supported by the circumstance that an anhydrous distillate is not precipitated by hydrogen sulphide unless decomposition has first been set up by the addition of water.

If the methylic solution of arsenic acid saturated with hydrochloric acid gas (0·2 to 0·3 grm. As_2O_5, in 40 to 50 c.c. $CH_3.OH$) is heated in a distillation flask on the water-bath, arsenical vapours are given off at 40° to 50° (thermometer in the flask), the main quantity following at 65° to 90°. A repetition of the operation yields only small quantities of arsenic, and on a third distillation the contents of the flask and the distillate are usually free from arsenic.

As the distillatory method it is convenient to use a round flask holding 250 c.c., which can be closed by means of a cap, ground to fit, and melted on to the condenser. Through this there passes (ground to fit) a dropping-funnel, which reaches almost to the bottom of the flask. The liquid distilling over flows into a flask of the capacity of about ¾ litre through a tube, ground in as a stopper and extending to the middle of the flask, and also ground to fit the outflow of the refrigerator. Laterally, on the neck of the flask, there is a ground junction for a three-ball receiver.

In carrying out the distillation we proceed as follows:—

The solution of the substance to be analysed is mixed in the distillatory flask with 50 c.c. methylic alcohol, as nearly anhydrous as possible, and, after the reception flask has been charged with 20 c.c. of concentrated nitric acid and the three-ball receiver with distilled water, the development of hydrochloric acid is introduced, in order to prevent the reflux of the methylic alcohol.

The dropping funnel certainly serves for the reception of the re-ascending methylic alcohol, but in some cases the liquid may spirt over into the dry bottle between the generating flask and the distillatory vessel, if the cock of the funnel is not closed soon enough. The distillation flask is kept cool by means of cold water, as otherwise the methylic alcohol might be heated to ebullition in consequence of the absorption of the hydrochloric gas. After complete saturation it is distilled off from a water-bath, whilst a very weak current of hydrochloric gas is kept up.

According to the quantity of the arsenic acid the distillation must be repeated once or twice, or even three times if the methylic alcohol has been diluted with much water. To this end the funnel cock is closed, the distillatory flask is refrigerated, the dropping funnel is filled with the corresponding quantity of alcohol, which is allowed to flow into the distillation flask.

When all the arsenic has passed over the contents of both receivers are transferred to a porcelain capsule holding 1 litre, and the receivers are rinsed out with water, covering the capsule with a clock-glass on account of the rather brisk development of gas. After the addition of 20 to 30 c.c. of concentrated nitric acid it is heated on the water-bath, keeping the capsule covered with a clock-glass until the violent escape of chlorine has come to an end. The liquid is then evaporated down to 100 c.c. After again adding an equal quantity of nitric acid, and complete evaporation, the residue is taken up with water, filtered, and precipitated with magnesia mixture.

II. *Distillation of Pure Arsenic Acid.*

Weighed portions of pure arsen-trioxide were oxidised to arsenic acid by means of concentrated nitric acid, the solution completely evaporated down, the residue mixed with water into the distillation flask, the water evaporated down to 5 to 10 c.c., and generally a threefold distillation is effected with 50, 40, 30 c.c. of methylic alcohol. The fourth distillate and the residue were always tested, and found free from arsenic.

III. *Separation of Vanadic Acid and Arsenic Acid.*

A direct separation of arsenic from vanadic acid has hitherto been practicable only by reducing the latter to V_2O_4 by boiling with SO_2, and precipitating the arsenic by sulphuretted hydrogen under pressure, re-oxidising the vanadium in the filtrate, and, according to the nature of the base present, separating with $HgNO_3$ or other agents, or titrating in the reduced solution with permanganate.

For the experiments we used ammonium vanadate, $AmVO_3$, repeatedly re-crystallised, and containing 77·82 per cent V_2O_5, and pure arsenic acid.

On distilling $AmVO_3$ alone with methylic alcohol and hydrochloric acid, there passes over firstly a dark liquid containing vanadic acid. By degrees the distillate becomes lighter, and finally clear as water, whilst the colour of the liquid in the distillation flask changes from dark brown to a blue-green.

If 20 c.c. of water are added to the methylic alcohol only the first drops of the distillate have a violet colour. To prevent this the vanadic acid, *before* the addition of methylic alcohol, is reduced by heating with a little sulphurous acid, when the distillate is from the commencement clear as water, and contains no vanadic acid.

Before the second distillation of arsenic the water remaining in the flask is evaporated away as far as possible, since a volatilisation of vanadium is no longer to be dreaded.

In the following analyses the distillation was repeated four or five times, using at first 50 c.c. and afterwards 30 to 40 c.c. of methylic alcohol.

For determining the vanadic acid in the residue the contents of the flask were rinsed into a porcelain capsule by means of nitric acid, evaporated to dryness, transferred with ammonia into a weighed platinum capsule, and after evaporation and ignition the weight of the vanadic acid was determined.

IV. *Separation of Arsenic and Molybdic Acids.*

In the analysis of their alkaline compounds these arsenic and molybdic acids are generally separated by supersaturating the solution with ammonia and adding magnesia mixture. The precipitate of ammonium-magnesium arseniate thus obtained is allowed to stand for forty-eight hours, and filtered, dissolved in nitric acid, again precipitated with ammonia, and converted into magnesium pyroarseniate.

To the collected filtrates are added ammonium sulphide and sulphur, and the molybdenum sulphide precipitated by acid is converted into disulphide or metal by reduction in a current of hydrogen.

Though this method, on account of the ready entrance of molybdic acid into the double magnesium salt, does not give the most accurate results, it is still preferable to an indirect method in which both acids are precipitated together as mercury salts and ignited in a current of hydrogen. The arsenic then escapes and the molybdic acid is reduced to metal, but a part of the molybdenum is apt to be volatilised, and, on the other hand, its complete reduction is difficult to effect.

The authors' experiments were made with ammonium paramolybdate, three times re-crystallised, containing 81·55 per cent MoO_3.

This salt, on distillation with anhydrous methylic alcohol and hydrochloric acid, behaves similarly to ammonium vanadate, but an addition of water is here sufficient to prevent molybdenum from passing over.

For the management of the distillation everything holds good which has been said concerning vanadic acid. The determination of the molybdic acid in the residue is effected in the manner described for vanadic acid. But the temperature must not be raised to redness. Hence the residue of evaporation is dissolved in ammonia and filtered into the platinum capsule, in order to remove the carbonaceous matter derived from the alcohol.

V. *Determination of Arsenic Acid and Tungstic Acid.*

The separation of arsenic acid from tungstic acid involves the greatest difficulties, as the former cannot be entirely removed by ordinary precipitants, nor even by sulphuretted hydrogen under pressure.

It is best to follow Kohmann's directions, boiling the salt in question for half an hour with the double calculated weight of soda-lye, in order to split up the two components, and then with twice as much ammonium chloride as is necessary to combine with the alkali present; $\frac{1}{4}$ vol. of ammonia and magnesia mixture are added: the mixture is filtered after the lapse of two hours, washed with a mixture of ammonia and ammonium nitrate, and the precipitation is several times repeated. Certainly the total quantity of the tungstic acid can scarcely be separated from the ammonium-magnesium arseniate.

The collected filtrates are evaporated down with hydrochloric acid when the quantity of magnesium salt has a very disturbing effect.

We succeeded in the following manner in separating both acids with great accuracy:—

The principle of the method is that we determine in one portion of the substance the joint weight of both acids, and in a second the weight of the tungstic acid alone, and calculate the arsenic acid from the difference.

As we find, the determination of the total weight can be thus accurately effected:—The aqueous solution of the arsenic tungstate is heated on the water-bath, and whilst diligently stirring a solution of mercurous nitrate is added until no further precipitation takes place, whereupon the free nitric acid is neutralised by pure mercuric oxide suspended in water. After heating the whole (still covered with a clock-glass) for twenty minutes on the water-bath, it is allowed to cool, the precipitate is filtered off, washed with water containing nitric acid, dried, removed from the filter as completely as possible, and the rest still adhering to the paper is dissolved into a platinum crucible with warm dilute nitric acid. After evaporating away the acid the bulk of the precipitate is introduced into the crucible, covered with a large quantity (15 to 20 grms.) of weighed, anhydrous, normal sodium tungstate; the crucible is filled with water and evaporated to dryness on the water-bath, whereby the precipitate is intimately pervaded by the sodium tungstate.

The covered crucible is then gradually heated to 200° in the air-bath—whereby the rest of the water escapes—and cautiously ignited (under the draught-hood), first with a single burner, and then with a sixfold burner. A constant weight is obtained after a single ignition for half an hour.

The filter, to which a small quantity of tungstic acid still adheres, is burnt separately.

For determining tungstic acid alone, the precipitation and drying of the precipitate are effected exactly in the same manner, but, after its removal from the filter, the latter is burnt at once without a previous treatment with nitric acid; the main quantity of the precipitate is added, and ignited at once with the addition of the normal sodium tungstate.

The results obtained possess an exactitude which is not even remotely approached by any other method of determination. The analyses are also convenient and expeditious in execution, and gain further in simplicity if, in determining the tungstic acid, we use the Gooch crucible and thus dispense with the incineration of the filter.

The above method of the distillation of arsenic with methylic alcohol in hydrochloric acid is available also for the separation of arsenic from many other elements, especially from iron, cobalt, nickel, and copper, which it accompanies in numerous minerals.—*Berichte*, xxviii., p. 1414.

Synthesis by means of Cyanacetic Ether. — T. Klobb.—In this manner the author has obtained the phenacylcyanacetic and phenacylacetic acids and the methylmethyl phenacylcyanacetate and the analogous ethyl compound. He has also studied the action of chloracetone upon sodium cyanacetic ether.—*Comptes Rendus*, No. 14.

THE SCIENCE OF EXAMINING.

By PETER T. AUSTEN, Ph.D., F.C.S.

Much severe criticism is being directed against examinations and much of it is timely and fully deserved. And yet when the criticisms are carefully considered they appear to be directed not so much against examinations as a method in education as against certain forms of examinations which are very prevalent and which certainly do not show anything more than evanescent memorisation, adroitness, or trickiness on the part of the student. No one will deny, however, that much of actual life is a kind of examination, and that we are being continually pressed to solve problems of all kinds, apply knowledge, and in general to act, and that on the success of our efforts will depend the positions we will attain, or at least maintain. There seems to be no reason why examinations should not be made an extremely important part of education, instead of being, as I fear they often are, an unmitigated nuisance to both student and teacher, a bone for the pedagogical critics continually to snarl over, and, when all is done, to be of no real use to either teacher or student, and to show nothing as to the real nature of the teaching done and the mental development of the student.

For the teacher who teaches from love of teaching, and who knows that successful teaching calls for the application of psychological principles far more than is generally supposed, there is a peculiar fascination in an examination paper. An examination may be made a test of the contents, capacity, quality, and action of a mind under defined conditions; but the paper must be a good one; I do not refer to the work of an inexperienced hand. The idea seems to be prevalent that anyone can write an examination paper. This is a great mistake. The elaboration of a paper that will really test not only the contents of the mind, but also its different functions as developed by a particular study under the guidance of a particular teacher, requires experience and ability. It is true that a man may be a good teacher and a poor examiner, but this usually arises from a lack of attention to the science and art of examining. My experience in this branch of pedagogical science leads me to believe that there are not very many really good examiners, and that the average examinations do not test the minds of the students as they ought to be tested. The average examination calls mainly for an exercise of memory, and for some proof that the student understands the matter he has studied. No man values the faculty of memory more highly than I do, or requires a better understanding of a given subject. But memory and mere understanding are only the foundations of education. More than this is called for. Some examinations require skill in observation, others accurate definition; while others bristle with problems. Some call for knowledge in which the teacher is weak. Almost every pedagogic earmark may be found in examination papers, but rarely is the paper constructed on such a plan that it tests not only the quality and quantity of knowledge in the mind, but also the various workings of the mind, and ascertains what the mind can do when set in action by the particular subject.

In my own speciality of chemistry there is an excellent opportunity for examination papers which may test the mind qualitatively and quantitatively, and probe both absorptive and productive powers. I have always taken a great interest in working out examination papers and in studying the minds as they appear in the answers. I am accustomed to work out questions under various heads. The following example will serve to indicate my meaning, and may also encourage others to experiment in examinational science; and I think that the method will be found so interesting that the investigation will not be hastily dropped. I should add that in the examination paper as given to the students the questions are mixed up, so that the classifications given as follows do not appear.

Questions for Testing:—

Memory.—(1) Give a brief history of oxygen. (2) Outline the theory of phlogiston. (3) What are "copperas," "bluestone," "tincal"?

Accuracy of Definition.—(4) State concisely the laws of Dalton, Charles, Mariotte, and Avogadro. (5) Define a mechanical mixture. (6) Define an element.

*Observation of Experimentally Demonstrated Facts.**—(7) Describe and sketch an apparatus for producing acetylene from calcium carbide, and explain the working of it. (8) Describe and sketch the combustion of nitric acid in iodohydric acid.

Accuracy of Detail.—(9) Explain with the aid of sketches the reduction of hot cupric oxide by hydrogen, heating the oxide in a combustion-furnace and preparing the hydrogen in a Kipp generator.† (10) Make a sketch of a section of Pepy gasometer, and explain how the apparatus works.

Acquaintance with the Properties of Matter.—(11) Describe the properties and chemical behaviour of nitrogen, sulphur, zinc, silica, and iodine.

Retention of Oral Instruction.—(12) Explain the contamination of water by sewage. (13) Describe the process for making open hearth steel.

The Faculty of Comparison.—(14) State similarities and differences between the properties of oxygen and hydrogen. (15) What substances resemble lead sulphide in colour and solubility in nitric acid?

Lucidity of Statement.—(16) Describe minutely and without sketches the apparatus and method of preparing phosphine. (17) Prove by analysis of stibine by volume that the molecule of antimony is tetratomic.

Recognition of Substances.—(18) A yellowish green gas with a suffocating odour. What may it be? (19) A colourless gas, very soluble in water, gives white fumes with hydrochloric acid. What may it be? (20) A white powder, insoluble in water; heated with concentrated nitric acid it evolves red fumes and yields a solution, which, when excess of acid is evaporated off, and it is diluted with water, yields a precipitate which is insoluble in concentrated nitric acid. What may this white substance be? (21) A chemist wishes to fill a jar with red liquid. What substance may he use?

The Ability to Observe.—(22) Give four examples of chemical change which you observe in this room. (23) Describe an ordinary red building-brick, stating dimensions and properties of surface, weight, fracture, &c. (24) Water expands on freezing. Give five examples of results caused by this expansion which you have personally observed.

The Application of Facts to Proofs.—(25) Prove that water is formed by the combustion of a kerosene lamp. (26) Prove that hydrogen sulphide contains sulphur.

The Interpretation of Phenomena.—(27) A piece of white paper on being held for an instant in the flame of a candle and at right angles to it, a black ring is formed on the paper. Explain what the ring indicates, and how the particles of carbon are formed, and why they are deposited on the paper. (28) A Roman candle on being ignited and then thrust under water continues to burn. How can this be accounted for? (29) Why cannot fish live in lakes on the tops of very high mountains?‡

The Application of Knowledge.—(30) The iodine falls into the sand box. How can the iodine and sand be separated? (31) A mixture consists of barium carbonate, sodium sulphate, and sulphur. How can they be separated? (32) A manufacturer has a waste product consisting of a liquid containing 40 per cent of sulphuric acid, 10 per cent sodium sulphate, and 5 per cent ferric sulphate. How can he treat it so as to convert it into other products that have commercial value?

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* Given in lectures and not in text-book.

† Given in text-book and demonstrated in lecture.

‡ Compare London University Matriculation Examinations, Stoker and Hooper, p. 31. Q. 6.

Deceptive or Misleading Questions.—(33) Dilute sulphuric acid is poured upon zinc. A gas with a slight bluish* colour is evolved, which burns with a red* flame. What is it? (34) Chlorine gas is collected in a jar over mercury† in the usual manner. It is then brought into a eudiometer, mixed with twice‡ its volume of hydrogen, and exploded. How many volumes of hydrochloric acid gas will be produced?

The Imagination.—(35) Filthy water of the gutter, warmed by the sun's rays, escapes from a foul environment, and, condensing, sparkles like diamonds on the petal of the violet. Use this as basis for an allegory in life.

These questions do not by any means represent all the possible divisions of mental action, and I have purposely avoided those of a very technical nature, most of which, however, would fall under the heads given; but they will serve to indicate what opportunities there are to construct examination papers that shall test a student's knowledge and the working of his mind. It may be urged against the questions I have given that several of them might fall as well under one head as another, or that a few more elaborate questions could be made out and each question marked under the several heads. My experience, however, has not been that the real ends are best attained in this way. The question that is distinguished by its definite nature and object gets a clearer answer and gives a more satisfactory insight into the student's mental equipment and action than a long or complicated one. If, after teaching a student a subject for a certain time, an examination shows that he can bring forth nothing more than that which has been put into him, it may be inferred either that the teacher is incomptent, or that the student is intellectually deficient; assuming, of course, that the system in the particular institution permits the teacher to do his best, does not assign him more pupils than one man can teach, and requires the student to do the work assigned to him. In such case I think that the fault usually lies with the teacher. Still I admit that there are institutions in which educational work of a high pedagogical order is impossible, and mind development, as distinguished from mind cramming, is out of the question. In such a case students are produced who are saturated with knowledge, but who are incapable of utilising it. Like water-logged vessels they roll about aimlessly, and are unable even to keep out of the way of craft which are taking the fullest advantage of wind and tide. In such an institution the earnest teacher, when he fails, deserves sympathy more than blame.

The results of examinations, conducted on some plan like the one I have attempted to describe, are very interesting. Such examination papers are far more difficult to write than the calls for mere memorisation that are so frequently made on the student, and which a hasty cram will enable a fairly bright candidate to pass. The answers are more difficult to rate; and often an attempt to mark them according to the usual rules is unsatisfactory. It is quite easy to assign a mark to the amount that a student knows, or even to discriminate as to the quality of his knowledge. To assign a figure to his ability to apply this knowledge, to originate, to create, to act under its instigation, is more difficult; yet it can be done with a fair degree of success.

It must always be borne in mind that a man's value in this life does not depend merely on what he knows, but upon what he can do. *Cæteris paribus*, the more he knows, the more he should be able to do; for so much the greater should be the incentive, if the knowledge imparted to him acts on him as it should. Until technical education was introduced, this fact was not well understood, and it is still far from appreciated in many schools.

For instance: A shows in his paper an encyclopædic knowledge. In his answer to Q. 11 he recites with great precision the properties of silica and iodine. But he fails to answer Q. 30, which calls for a conclusion dependent upon this knowledge. He is like a recruit who has been given a gun, but has not been taught how to fire it off. Such a student demands the teacher's attention at once, His mental inaction is usually the result of poor teaching.

It may not be amiss for me to say parenthetically here that teaching is the most difficult of all professions. It is not usually regarded so, but I believe that it is. Much of what is called teaching is nothing more than a kind of pumping. Knowledge is forced in through the most convenient intellectual orifice, a great deal being lost *in transitu*, and not a little leaking out afterwards. The engorged recipient is like a boiler whose feed-pump is too big for it and will not cease pumping, but fills the boiler entirely full of water and leaves no space for steam; whereon the engine slows down and stops, or throbs soggily with its cylinder filled with lukewarm water instead of hot expansive steam.

Again, a student may fail in his attempts to state anything correctly or exactly; but he fills pages with attempts to apply his knowledge, suggesting all sorts of ideas and applications. Most of them may be impossible, some even ridiculous. But no matter, let the teacher take hold of this boy at once, for the mind of an Edison, a Siemens, or an Ericsson may be seeking nourishment and development. Happy is the teacher who can discern what mean the instinctive strugglings of the embryonic master mind, and who can liberate it from the thraldom of routine—who can guide its first weak attempts to walk and climb, until it becomes hardy and venturesome, and fearlessly scales cliffs heretofore inaccessible: and so clambering by hitherto unknown ways to the peak discovers new fields for human activity, and cuts a wide path by which thousands may enter and take possession.

What man gets closer to the Creator than the teacher, who can discern and understand His idea as shown in the youth and who clears away the obstacles in the way of its development, nourishes it until it is strong and independent, and itself becomes creative? Verily such a teacher has his reward.

Examination papers constructed on the basis I have suggested, viz., to test not only the knowledge possessed by the student, but also the working of his mind upon the particular subject, will show more clearly the nature and condition of a mind than the daily recitation, because the case is more capable of systematic study and can be made to cover larger fields of mental activity. While I do not intend to suggest that such examinations should replace the regular recitation, I believe that they should be held frequently, and should serve a far wider purpose than that of merely noting the quantity of knowledge absorbed by the mind. Such an examination is not a mere matter of testing and registering; it is a creative exercise of the mind.—*Science.*

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* Colourless.
† Chlorine cannot be collected over mercury.
‡ Once.

THE PRECIPITATION AND GRAVIMETRIC DETERMINATION OF CARBON DIOXIDE.*

By F. A. GOOCH and I. K. PHELPS.

The method upon which reliance is most confidently placed for the determination of carbon dioxide in solid carbonates, involving as it does the liberation of that gas by the action of a strong acid and its absorption in weighed potash bulbs, demands as conditions of the attainment of good results the careful observance of precautions and the expenditure of much time and attention. In the method described below we have sought to secure equal accuracy with greater economy of time and care.

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* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. l., Aug., 1895.

Our plan is to effect the rapid absorption of the carbon dioxide, evolved by the action of acids upon carbonates, in barium hydroxide contained in a specially devised apparatus, to filter and wash the precipitated barium carbonate under a protecting layer of xylene, to dissolve in hydrochloric acid the washed carbonate upon the filter or adhering to the receiver, to convert the barium chloride thus obtained into the form of the sulphate, and from the weight of the last to calculate the carbon dioxide originally liberated by acid from the carbonate.

The apparatus which we use, and which is shown in the figure, consists of a flask for the evolution of the carbon dioxide, properly connected with a receiver in which the gas is retained until absorption is perfect. It is a form of a similar device employed by one of us (*Amer. Chem. Journ.*, i., 450) for the absorption of ammonia in hydrochloric acid and the complete retention of the ammonium salt thus formed, but so modified as to avoid the danger of diffusion of carbon dioxide through the rubber balloon—a source of error which we have found by experiment to be considerable when large amounts of the gas are handled.

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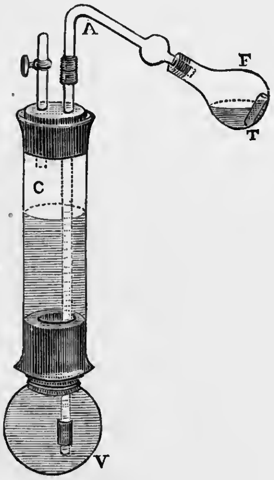

The evolution flask (F) has a capacity of about 50 c.m.^{3}, and is fitted with a rubber stopper through which passes a tube (A) wide enough (about 0·7 c.m. in interior diameter) to prevent the formation of bubbles, and expanded just above the stopper to a small bulb. The absorption cylinder consists of a wide glass tube (C), fitted at either end with a rubber stopper. The stopper at the lower end of the cylinder, placed vertically, carries a short tube, about 1·5 c.m. in diameter, to which is secured a smaller rubber balloon. The cylinder and balloon together hold about 100 c.m.^{3}. The upper stopper is perforated with two holes, through one of which passes the tube of a glass stopcock, while through the other hole passes a long tube reaching to the interior of the balloon and provided with a valve (V)—preferably a modified Bunsen valve, of the pattern recently devised by Kreider (*Am. Journ. Sci.*, l., p. 132).

In using this apparatus a saturated solution of barium hydroxide (which is made hot, filtered into a syphon-bottle, and preserved from atmospheric action by a floating layer of kerosene) is introduced by pressure upon the air in the syphon-bottle or by suction applied to the stopcock of the cylinder. Such a solution contains about 5 per cent of its weight of the hydroxide, and we find it best to use in every case an amount at least a fourth in excess of the quantity theoretically required to absorb the carbon dioxide, and to fill the cylinder and balloon nearly full of liquid. The carbonate is weighed, introduced into the flask, and washed down with 15 or 20 c.c. of boiled water, which is protected in the wash-bottle from carbon dioxide in the breath by a balloon attached to the inlet tube. A small tube, holding enough hydrochloric acid to effect the decomposition of the carbonate to be analysed, is placed in upright position in the evolution flask. The stopper is inserted in the flask, and connections are made as shown in the figure; the little tube containing the acid is overturned by inclining the flask; the acid mixes with the water, and effervescence begins. Heat is applied, and the liquid in the flask is boiled until that in the cylinder is heated by the steam nearly to the boiling-point, in order that the precipitated barium carbonate may become as granular as possible. The carbon dioxide evolved and the air in the flask are transferred in the process to the absorption cylinder, the valve serving to prevent the back flow of the liquid, while the balloon expands to give room to the air and condensed steam. When the boiling is done the flask and tube are disconnected at the rubber joint, the cylinder is shaken to insure the absorption of the carbon dioxide, and the liquid carrying the greater part of the precipitate is transferred through the stopcock to a filter carefully fitted to its funnel, moistened with water, and containing about 5 c.m.^{3} of xylene (which we found to be preferable to benzene, kerosene, or amyl alcohol), the function of which is to rise to the surface when the aqueous solution is added, so as to protect the barium hydroxide from the action of the carbon dioxide of the air. By manipulating the balloon and the stopcock (to which a little funnel may be attached by a piece of rubber tubing for convenience in introducing wash-water) the cylinder may be emptied and washed out with hot boiled water, though, of course, a very considerable portion of the precipitate remains adhering to the walls of the absorption apparatus.

We prefer to prepare the filter for use with the suction pump, but in the early stages of filtration and washing very little suction should be applied. When the barium hydroxide has been nearly washed out of the precipitate, the xylene is dissolved in a little hot alcohol, the suction is applied, and the washing is completed with hot water. The emulsion of xylene and water found in the filtrate is readily cleared up by alcohol. Finally, the barium carbonate in the absorption apparatus and upon the filter is dissolved in hydrochloric acid and precipitated in hot solution by sulphuric acid; the resulting barium sulphate is filtered, washed, and ignited upon asbestos in a perforated crucible, and from its weight the carbon dioxide which originally precipitated the barium, now in the form of the sulphate, is calculated, The results of a series of determinations made in this manner are recorded in the following table:—

(Ba=137·43, S=32·06, O=16, C=12.)

$CaCO_3$ taken. Grm.	$BaSO_4$ found. Grm.	CO_2 actually present. Grm.	CO_2 calculated. Grm.	Error in CO_2. Grm.
0·0500	0·1180	0·0220	0·0222	0·0002 +
0·0500	0·1183	0·0220	0·0223	0·0003 +
0·1000	0·2329	0·0440	0·0439	0·0001 −
1·1000	0·2347	0·0440	0·0442	0·0002 +
0·2000	0·4660	0·0880	0·0878	0·0002 −
0·2000	0·4653	0·0880	0·0876	0·0004 −
0·5000	1·1650	0·2200	0·2196	0·0004 −
0·5000	1·1657	0·2200	0·2197	0·0003 −
1·0000	2·3323	0·4400	0·4396	0·0004 −
1·0000	2·3309	0·4400	0·4394	0·0006 −

Various modifications of method and manipulation were put to the test of experiment, but the process which we have described has proved on the whole the most satisfactory. It is fairly rapid and accurate.

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Continued from p. 184).

Choice and Purification of Liquids.

As stated previously, the liquids employed in the course of this investigation were those recognised to be strictly normal; and of those only such were chosen as can be gotten in a state of great purity. The only associated liquid taken was acetic acid, whose degree of association as well as whose physical properties are to a certain extent known.

An associated liquid was investigated for the purpose of applying the regularities and "normalities" discovered in mixture of normal liquids to mixtures of a normal liquid with an associated liquid. Great pains were taken to purify the liquids in the highest possible degree, it being the testimony of all those who have occupied themselves with experimental work on the vapour-tensions of liquids that even very slight impurities have a remarkably disturbing effect upon the accuracy of results; this is especially the case in results obtained by the static method; in the method employed by me, the influence of a slight amount of impurity is not so marked; still, for all that, it has been thought best to employ such material as had been most thoroughly purified.

In order that the readers of this paper may judge for themselves the degree of purity of the liquids examined, a somewhat detailed account of the method of purification of each liquid is given together with a statement of certain characteristic physical properties of each. All of the liquids, it may be stated beforehand, were bought as chemically pure from the dealers (Poulenc Frères, Paris, and Billault, Paris), and at least one pound—generally two or three pounds—subjected to the purifying operations.

Benzene.—Nearly three pounds of benzene—labelled chemically pure and free from thiophene—were treated a half-dozen times with sulphuric acid to remove last traces of the sulphur compound. The liquid was then repeatedly fractionally crystallised until about a pound was obtained melting at 5·3°. This purified product when partially solidified showed, no matter what the proportion of liquid and solid was, the same melting point. The whole was then distilled over a few pieces of sodium, no variation from the boiling-point 80·1° under a pressure of 756 m.m. of mercury being observed. Its specific gravity at 25° referred to water at the same temperature was found to be 0·876611.

Toluene.—Of the quantity of toluene taken for purification (about two pounds) more than four-fifths distilled at 109·8° to 110·1°, an indication that the commercial article was nearly pure. After a couple of distillations over a little sodium, more than a pound was obtained boiling constantly at 110·1° under a pressure of 758 m.m. of mercury. Its density at 25° referred to water at 25·0° was ascertained to be 0·86288.

Monochlorbenzene.—A couple of pounds of monochlorbenzene were repeatedly distilled in fractions until a constant boiling product resulted. About three-quarters of a pound were obtained, boiling at 131·8° to 131·9° under a pressure of 757 m.m. of mercury, and having a density of 25·0° (referred to water at same temperature) of 1·10362.

Monobrombenzene.—Nearly a pound of brombenzene was fractionally distilled until a distillate was obtained boiling between narrow limits. About 150 grms. of the product, boiling at 154·3° to 154·5° under a pressure of 761 m.m. of mercury were obtained. The density at 25° referred to water at 25·0° was 1·49852.

Nitrobenzene.—The commercial article was repeatedly crystallised until an almost colourless liquid was obtained, which, when solidified, showed the same temperature during the re-melting. It possessed a melting-point of 3·6°, and its density was 1·20201—

$$\left(\frac{25^\circ}{25^\circ}\right).$$

Chloroform. — About two pounds of "chloroform anesthétique" of commerce were washed a dozen times with water, dried thoroughly by means of fused calcium chloride, and distilled. The larger distillate boiled at 60·8° to 61·0° under a pressure of 751 m.m. of mercury; and, finally, nearly a pound was obtained boiling at 60·9° under a pressure of 755 m.m. of mercury.

Carbon Tetrachloride.—Two pounds were washed with water, and thoroughly dried by means of concentrated sulphuric acid. The product was then rectified, and nearly a pound boiling throughout the operation at 76·6° under a pressure of 756 m.m. of mercury taken for the preparation of the mixtures. The specific gravity of this product at 25·0° referred to water at the same temperature was 1·58828.

Acetic Acid.—Two pounds of glacial acetic acid were repeatedly fractionally crystallised until a portion melting at 16·7° was obtained. The bottle containing it, as well as the mixtures made from it, were kept under an air-tight bell-jar by the side of very strong sulphuric acid.

Preparation of the Mixtures.

The mixtures were prepared by weighing out to a milligrm. on a balance turning with a tenth m.grm. the liquids in a flask; the corked flask was tared, the less volatile liquid poured in and weighed, and then the more volatile. As from 40 to 100 grms. of the mixture were weighed out, the composition of the mixture was thus known to a ten-thousandth at least. The mixtures were preserved in bottles or flasks fitted with the finest corks, and kept in a dry cool dark closet. As, almost invariably, the necessary vapour-tensions of a liquid were made immediately after its preparation, no change of concentration occurred even with the most volatile liquids employed.

In the case of some of the mixtures of benzene and carbon tetrachloride, the residues of the investigated mixtures were united, and the amount of chlorine in the resulting mixture determined according to Carius's method.

The mixtures of benzene or toluene with acetic acid had their concentration controlled by an analysis. 5 to 10 c.c. of the mixture were carefully weighed out in a glass-stoppered flask, water was added, which took practically all the acetic acid from the benzene, and then standardised baryta-water run in to point of neutralisation. In no case did the analysis give results sensibly different from those calculated from the direct weighings.

(To be continued).

NOTICES OF BOOKS.

Elements of Modern Chemistry. By Charles Adolphe Wurtz. Fifth American Edition, Revised and Enlarged. By W. H. Greene, M.D., and H. F. Keller, Ph.D. (Strassburg). With a Portrait of the Author and numerous Illustrations. Philadelphia and London: J. B. Lippincott Company. 1895. Pp. 808.

In examining this work, we have firstly to consider the original as it issued from the pen of the late illustrious Prof. Wurtz, and secondly the version executed by Messrs. Greene and Keller.

The original must be recognised as an admirable summary of chemical science down to the death of the author (1884). Though it was more especially adapted to the requirements of medical students, it may be recommended as one of the best elementary works on chemistry of a

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* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

moderate compass. Professor Wurtz does not discuss the nature and possible origin of the elements; he gives them his provisional acceptance without speculating on their possible ultimate nature. Hence Prout's hypothesis is ignored, and the periodic classification of the elements with its consequences is ascribed exclusively to Mendeleeff, without any reference to Lothar Meyer or Newlands.

As many discoveries of the highest importance have been effected within the last twelve years, the task of the translators has not been easy. They have added notices of the isolation of fluorine, of argon and helium, of hydrazine, hydrazoïc acid, and their principal derivatives, of stereoisomerism, and of some of the more recent discoveries in the chemistry of the rare earths. The localities occasionally given, *e.g.*, for the occurrence of mineral waters, are almost exclusively American and little known to European readers. The language employed is not in all cases idiomatic English as spoken to the east of the Atlantic, but a moment's reflection enables the reader to detect the meaning.

The work before us deserves an honourable position in the library of the chemical student.

On Dangers to Men Employed in Chemical Works, Means of Preventing Accidents, and Conditions of Work. A Critical Discussion of English and German Industrial Relations, occasioned by the English Parliamentary Report of 1893. ("Ueber Gefahren für die Arbeiter in Chemischen Fabriken, Unfallsverhütungsmittel und Arbeitsbedingungen Eine durch den Englischen Parlaments bericht von 1893, veranlasste kritische Besprechung Englischer und Deutscher Industrie verhaltnisse"). By Konrod W. Jurisch, Docent at the Royal Technical High School of Berlin. Berlin: R. Gaerntner. 1895.

The report presented by the Chemical Works Committee of Enquiry of 1893 is, of course, well known in this country. Still, it is interesting to see how its conclusions and recommendations appear to a foreigner who has the advantage of personal acquaintance with the heavy chemical trades, and has resided for some time at St. Helens and Widnes. The Committee of Inquiry, unlike the late Rivers' Pollution Commission, had the advantage of including two physicians, whose special reports on the physiological actions of the conditions to which the workmen are exposed are eminently judicious.

As remedies for the effects of chlorine and of corrosive gases, the men have recourse to brandy or whisky. Dr. Jurisch found that they were ignorant of the employment of ammoniacal vapours, and could not be taught to use them. The present writer has often found personally and observed on others much benefit from sips of the strongest vinegar or dilute acetic acid. That Dr. Jurisch is closely acquainted with the effects of irrespirable gases is proved by the fact that he advises men in such cases to retire slowly, taking only slight superficial breaths of air until reaching a purer atmosphere. To take a full breath is exceedingly hazardous and might conceivably be fatal. The fact that certain precautions in vogue on the Continent are neither practised in English chemical works nor proposed by the Commissioners, Dr. Jurisch ascribes to the different conditions of work, and, above all, to the carelessness of the men and their aversion to be taught anything. He points out that the administration of ammonia to a man half suffocated with chlorine unless effected with judicious care may increase the mischief.

To a careful sober man the manufacture of chloride of lime presents far less dangers than has been represented by sensational writers. It is shown that relatively shallow layers of lime in the chloride chambers, which do not require to be turned over, are in reality preferable, as well from an industrial as from a hygienic point of view.

Small quantities of hydrochloric acid in the air do not interfere with respiration, improve the appetite, and occasion no inconvenience beyond "setting the teeth on edge." Vapours of sulphuric acid are more pernicious. It is remarked that boys under eighteen years of age are not employed in the manufacture of chloride of lime and of sulphuric acid, and that women are altogether excluded.

Caustic soda presents its dangers; a fall into the melting-pans is almost inevitably fatal. Hence it would be well if care were taken in British works, as in those of France and Germany, to exclude any man from work in this department who is not sober.

It is here remarked that in Continental works the mixture of lime-water and linseed oil, invaluable as a remedy for burns, is kept ready for use on a large scale. In England and Scotland it has been in use to our certain knowledge since 1857, under the name "Carron oil." The Commission did not think it necessary to mention so well known a remedy.

The use of lead acetate as an application to the eyes in case of a spirt of acid or alkali dates back to the same year, and that at a works in Widnes which certainly made no speciality of care for the sanitary well-being of the workmen.

This Report, both in its original form and in the German annotated and critical version, will be of great service in leading to hygienic improvements which can be introduced without interference with the manufacture.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 14, September 30, 1895.

The Death of Louis Pasteur.—A. Cornu, the President, delivered an eloquent discourse on the eminent merits of the discoverer whom the world, and more especially France, has just lost.

Remarks on the Discourse of Lord Salisbury on the Present Limits of our Science.—Emile Blanchard.—In the shape of a notice of the Presidential Address delivered by the Marquis of Salisbury at the Oxford Meeting of the British Association (1894), M. Blanchard has repeated the threadbare challenge of the anti-evolutionists, that if anyone will show an instance of the transformation of a species he will confess himself mistaken! He knows perfectly well that his challenge presupposes the impossibility of a naturalist living and observing for a few thousand years.

New Nitrogenous Manure: Calcium Cyanate.—Camille Faure.—The substance in question is calcium cyanate, $Ca(CNO)_2$, hitherto a laboratory curiosity, but now promising to become an important substitute for nitrate of soda, and even containing a larger proportion of assimilable nitrogen. A mixture of limestone and coke is submitted to a preliminary temperature of 1500° in an electric blast furnace, and is then superheated in the same furnace to 2500° in presence of a large excess of pure nitrogen, and finally to oxidation by means of air, the oxygen of which is retained by the product, whilst the nitrogen conveys the heat due to the oxidation into the electric chamber. The operation must be conducted in a large furnace, so that the calorific yield may be sufficiently economical. The assimilation of the nitrogen of this product by vegetation does not appear to be doubtful.

Constitution of the Acids produced in the Oxidation of Inactive Campholenic Acid.—A. Béhal.—The author claims the priority of the synthetic preparation of dimethylglutaric acid as against Dr. Tiemens.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 10, 1895.

Tinctorial Properties of Glucina.—M. Prudhomme. The author explained the different tinctorial properties of sesquioxides and protoxides. The former do not become saturated with alizarin in distilled water; in order to form a solid lake they require the co-operation of lime. The second dye up equally well with or without lime. Glucina as regards dyeing behaves like a protoxide.

Ammonium Manganous Phosphate, and its Use in the Volumetric Analysis of Phosphoric Acid.—MM. Lindemann and Motten.

Preparation of Monomethylamine.—A. Brochet and R. Cambier.—The authors place 2 kilos. of commercial formic aldehyd in a three-litre flask, connected to a good refrigerator by a Wurtz tube fitted with a thermometer, and 1 kilo. of ordinary crystalline sal-ammoniac. On heating gently the liquid becomes strongly acid and takes a yellow colour. At 40° there is produced a brisk ebullition, when the heat is reduced. Methylal distils over in abundance. We then raise the temperature by degrees to 95°. The receiver is changed and the distillate contains 60 to 70 per cent of methylal. The solution is concentrated until the excess of sal-ammoniac begins to precipitate, and on refrigerating this salt is deposited almost entirely. It is drained by suction; the filtrate is a solution of monomethylamine almost pure.

Two Combinations of Mercuric Sulphate with Thiophene, allowing of the Determination of this Substance in Commercial Benzines.—G. Denigès.—The author describes in detail the determination either in an aqueous or a methylic solution.

Ammoniated Derivatives of Hexamethyltriamidotriphenylmethan, its Carbinol, and its Mixed Ethers.—A. Rosenstiehl.—This voluminous paper does not admit of a complete abstraction. We may see that experimental proof is given that the leucobases, the magentas, and the rosanilines contain amidic-groups with the same functions. All three are triamines of the same degree; in all the three classes of compounds the three groups NH_2 fulfil the same functions without a single reaction leading to the admission that one of them is retained in the mol. of any other bond than that which retains the atom of H which it replaces in the mol. of phenyl.

The Question of Acid Magentas.—Maurice Prudhomme.—A polemical paper. The author considers that the conceptions on the nature of the acid magentas may thus be summarised:—1. The colouring and coloured matter exists as a neutral salt or an acid salt of the sulphonated carbinol. 2. The addition of a mineral acid to the salts of rosaniline liberates the latter, which is coloured.

No. 11.

Researches on Manganese.—Charles Lepierre.—Already inserted.

Hydrated Metallic Chlorides. A Reply to H. Lescœur.—Paul Sabatier.—A polemical paper.

Composition of the Wines of Samos used in the Manufacture of Vermuth.—P. Cazeneuve and M. Hugounenq.—A paper of no scientific interest.

Present State of the Production and Consumption of Phosphates.—David Levat.—A statistical account of the production of natural mineral phosphate in Florida, Carolina, Algeria, and Tunis, and of the phosphatic slags obtained by the Gilchrist process.

MEETINGS FOR THE WEEK.

Friday, 25th.—Physical, 5. "The Radial Cursor," by F. W. Lanchester. "The Development of Arbitrary Functions," by Prof. Perry and Mr. Hunt.

Erratum.—P. 185, col. 1, line 31 from bottom, *for* "0·47325 c.c." *read* "0·47325 grm."

THE CHEMICAL NEWS.

Vol. LXXII., No. 1874.

OBSERVATIONS BY AID OF THE TENSIOMETER.

By J. ALFRED WANKLYN and W. J. COOPER.

The paper which one of us prepared for (but did not read at) the Ipswich Meeting of the British Association (see Chemical News, vol. lxxii., p. 164) mentions our Tensiometer.

We employ two modifications of the instrument, viz., one modification designed for the measurement of low tensions, and another modification designed for comparatively high tensions.

The modification designed for low tensions is original only in some seemingly trifling details, which we hope to mention more particularly on another occasion. We confine ourselves at present to the publication of some of the earliest results which we have obtained.

Eleven consecutive terms of the Russian series of hydrocarbons, to which we have given the name kerose, as set forth in our recent papers on this subject, have been taken for investigation. Our results are as follows:—

Name of the hydrocarbon liquid.	Tension of the vapour evolved *in vacuo* at 15° C. M.m. of mercury.
Kerose xxiii.	1·2
„ xxii.	3·5
„ xxi.	6·9
„ xx.	8·9
„ xix.	10·0
„ xviii.	14·8
„ xvii.	18·0
„ xvi.	31·0
„ xv.	48·0
„ xiv.	59·0
„ xiii.	82·0

The first of these hydrocarbons boils under ordinary atmospheric pressure at 176° C., and the last at 76° C.; and it will be observed that the gradual drop in the boiling point is shadowed forth by a continual increase of the tension of the liquid at ordinary temperatures.

We have also measured the tensions of valerianic acid, acetic acid, and formic acid at 15° C. as follows:—

	M.m. of mercury.
Valerianic acid	6·0
Acetic acid	9·0
Formic acid	10·0

Now, valerianic acid has about the same boiling-point as Kerose xxiii., and acetic acid nearly the same boiling-point as Kerose xvii., and formic acid comes between Kerose xv. and Kerose xvi. There is utter want of parallelism between the fatty acid and the hydrocarbon in the matter of tension at ordinary temperatures.

Tension of acid.	Corresponding tension of kerose.
6	1·2
9	18·0
10	40·0

The drop from the boiling-point of valerianic acid to the boiling-point of formic acid is shadowed forth by the increase from 6 to 10. But among the keroses a like drop in boiling-point is indicated by the increase from 1·2 to 40·0.

The first term in our table of the eleven keroses has a tension of 1·2 m.m. at 15° C. If we gradually raise the temperature, the tension will gradually increase, attaining to 80 m.m. at about 96° C. When any of these keroses attain to a tension of 80 m.m., we are able to describe the comparatively steep section of the tension-curve with approximate accuracy. Given the point in temperature at which the tension attains to 80 m.m. we can name the boiling-point under ordinary atmospheric pressure. The rule is, add on 80° in the case of Kerose xxiii.; add on nearly 60° in the case of Kerose xiii., and add on intermediate numbers in the instance of the intermediate keroses.

THE LATEST DISCIPLE OF HERMES TRISMEGISTUS.

By H. CARRINGTON BOLTON.

The persistence with which a belief in the transmutability of metals clings to common people in these days of universal education shows that there are still individuals in whom avarice linked with superstition are stronger characteristics than honesty in thought and action. In France the publication of alchemical processes continues, scarcely a twelve-month elapsing without an addition to this literature; in that country, too, as well as in England, claimants of the secrets of Hermes occasionally appear. Often their first appearance in public takes place in a police-court to answer charges of fraud, for the law does not recognise the veridity of alchemical professions. The case of the ingenious American who endeavoured to swindle the Bond Street jeweller a few years ago, by borrowing gold sovereigns with a promise to "multiply" them, is fresh in the minds of readers of the Chemical News.

In September of this year an extraordinary exhibition of faith in alchemy occurred in New York City, the details of which remind us of similar transactions reported in the Middle Ages.

The persons in this domestic drama are four in number —a small tradesman, Gustav Hammer by name, and his wife, who became the dupes of two conspirators named Stanley Glass and Max Pearlman. In the spring of 1895 Glass confided to Hammer that a friend of his possessed a wonderful secret which would make them all rich; his friend, he explained, was an alchemist, and with a little brass, some copper, and a few platinum filings, and the wonderful secret, he could procure any amount of gold. These representations interested Hammer and his wife, who consented to go into the business. Soon after, Glass introduced his friend Pearlman as the possessor of the Philosopher's Stone, and these two induced Hammer to furnish the money necessary for an experiment; the latter gave the reputed alchemist 4.50 dols. for platinum and 234 dols. for other materials. After some delays and procrastination on the part of Pearlman, the great work was undertaken in his house.

The experiment was conducted in a semi-dark room, and began at midnight. The metals were placed in a crucible over a very hot fire, and Pearlman stirred them with a rod, at the same time pouring in a white powder —the Philosopher's Stone. The heat was maintained for a long time until the metals fused. After cooling the crucible, Pearlman took out the alloy and gave it to Hammer, saying it was pure gold. The tradesman took the fused mass to an assayer, who informed him the lump contained 18 dols. worth of gold.

So far this resembles a page from the career of Sendivogius, but the sequel is very different. Hammer, indignant at the swindle, sought relief in the courts, and on his representations the Grand Jury indicted Stanley Glass and Max Pearlman. During the taking of testimony, it appeared that Mary Pearlman, the alchemist's wife, had sought to have the case dropped by offering various sums of money—beginning with 60 dols. and rising to 100 dols. This was corroborated by Mrs. Louisa Hammer.

At the last accounts, Glass had been arrested, but Pearlman could not be found. Verily, the good old times of Cagliostro have departed!

QUANTITATIVE ANALYSIS BY MEANS OF ELECTROLYSIS.*

A PRELIMINARY report was furnished by the Committee last year in which the contemplated plan of work was outlined.

The bibliography of the subject has been completed and is appended.

The experimental work has been carefully organised, and the results on the determination of bismuth and of tin are nearly complete. Other work is in progress, but the Committee prefer to hold over these results until next year in order that they may be added to and may include methods of separation of some of the metals.

Considerable attention has been given to the choice and arrangement of the special apparatus required. A detailed description of some of the arrangements adopted will be given in the next report.

As the bibliography is completed, the Committee propose to devote their attention during the coming year exclusively to experimental enquiries.

Bibliography on Methods of Quantitative Analysis by means of Electrolysis.

The bibliography has been compiled from the following journals, and is complete up to the end of 1894:—

Journal.	Period abstracted.	Abbreviation.
1. Journal of the Chemical Society	1847-1894	J. Chem. Soc.
2. Journal of the Society of Chemical Industry	1882-1894	J. Soc. Chem. Ind.
3. Chemical News	1860-1894	Chem. News.
4. American Chemical Journal	1878-1894	Amer. Chem. J.
5. Journal of Analytical and Applied Chemistry..	1887-1894	J. Analyt. and App. Chem.
6. Journal of the American Chemical Society ..	1879-1894	J. Amer. Chem. Soc.
7. Zeitschrift für Analytische Chemie	1862-1894	Zeits. anal. Chem.
8. Berichte der Deutschen chemischen Gesellschaft..	1868-1894	Ber.
9. Zeitschrift für anorganische Chemie	1892-1894	Zeits. anorg. Chem.
10. Zeitschrift für physikalische Chemie	1887-1894	Zeits. phys. Chem.
11. Zeitschrift für Electrochemie. (Organ der deutschen electrochemischen Gesellschaft)	1894	Zeits. Electrochem.

References to papers of importance published in journals other than the above are also included.

Books of Reference.

1. "Quantitative Analyse durch Electrolyse." A. Classen. 3rd edit., 1892. Published by J. Springer, Berlin. Translation, by W. H. Herrick, of 2nd edition, 1887, "Quantitative Chemical Analysis by Electrolysis." Published by I. Wiley, New York.
2. "Electro-chemical Analysis." Edgar F. Smith. 1890. Published by P. Blakiston, Philadelphia.
3. "Jahrbuch der Electrochemie." W. Nernst and W. Borchers. 1894 (first year of publication).

Arrangement of Bibliography.

The bibliography is divided into the following sections:—

1. General conditions for electrolytic analysis.
2. Special apparatus employed.
3. Quantitative methods, for the determination of metals by means of electrolysis.
4. Quantitative methods, for the separation of metals by means of electrolysis.
5. Special applications of electrolysis in quantitative analysis.
6. Applications of electrolysis to qualitative analysis.

THE PERIOD-TABLE.*

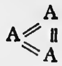
By F. RANG.

THE space in the Table between C, Si, and A, $_3$IV.*b*, is not a real one, but only an unavoidable defect similar to that encountered when a globe is mapped on a plane surface.

Every sign in this Table signifies not only its usual element, but also every other element in the same series, valency, and part of the Table. La and Yb signifies, therefore, La, Ce, Ny, Py, Sm, Tb, Ho, Er, Tm, Yb, and perhaps as many more yet unknown elements. Their atom-volumes and chemical activity show that they do not make a series.

Several facts indicate that H is here put in its right place. Now when A is found we no longer have any right to be incredible about the existence of the elements marked (+), and, moreover, we are able in some places of the Table to predict where they are to be found, *e.g.*, which elements the explorer could use as ores. We are also able in some degree to predict their general properties.

What is now known about A, together with its periodic arrangement, tells us that it has the molecule—



atomic weight 13, and valence IV. A glance at the molecular formula of A will explain its resistance to chemical action; its molecule is not easily broken, but when its atoms are once separated, it is likely to get an extended chemistry.

Table of Half-forgotten Elements.

	Atomic weights.		Reference.
	Probable.	Derivation.	Chem. News.
Davium, Da, sp. gr. 9·39	100	⅔ (150—154)	xxxvii., 65
Uralium, (Url), sp. gr. 20·25	187	187	lviii., 188
Norwegium, Ng, sp. gr. 9·44, m.-p. 350° C. ..	64	½ (145)	
Austriacum, (Ast)	212	212	lix., 295
Neptunium, Np	236	2 (118)	xxxv., 197
Ilmenium, Il	?	104·6	xxxv., 197
Polymnestum, Pm.. ..	?	74	Of the group Ti—W.
Erebodium, Eb	94·5	94·5	
Gadenium	?	43·5	
X, X' X"	?	?	

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* Read before the British Association (Section B), Ipswich Meeting, 1895. (Second Report of the Committee, consisting of Prof. J. Emerson Reynolds, Chairman, Dr. C. A. Kohn, Secretary, Prof. P. Frankland, Prof. F. Clowes, Dr. Hugh Marshall, Messrs. A. E. Fletcher, D. H. Nagel, T. Tnrner, and J. B. Coleman).

* See Chem. News, vol. lxvii., p. 178.

Valence. Series.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.			I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1.	..	..	..	..	..	..	..	..	..	..	..	..	H	He	*	(+)	(+)	(?)
2.	Li	Be	B	C	..	..	..	..	..	..	..	..	..	A	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	Da	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	(?)
6.	Cs	Ba	La	Yb	Ta	W	Url	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Ast	(+)	(?)
7.	(+)	Ms	(+)	Th	Np	U	(?)	(?)	(?)	(?)								

$_4$III.a = Sc, Pp. $_4$I.b = Cu, Ng. $_6$III.a and $_6$IV.a = La, Ce, Ny, Py, Sm, Gd, Tb, Ho, Er, Tm, Dc, Yb. . . .

* Unnamed element accompanying helium.

A most of all known substances violates Dulong and Petit's law, and also the general application of Avogadro's law; it has next to H the highest specific heat of all elements; its light-refraction is low in proportion to its specific gravity, but its *atomic volume* corresponds *exactly* to its place in the diagram of the atom-volume-series. (The atomic volumes for C, A, and N are 3·4, 8·7, and 15·5).

As some of the elements in my Table have not been introduced before in any period-table, and are therefore unknown to many, I have, for what good it might be, put together the Table in preceding column.

The sp. gr. of Da and Url give a peculiar and verifying shape to the corresponding parts of the diagram over the atom-volume-series. Probably He and its side-elements give similar diagram verifications.

I claim that my period-table is the truest and best tabular arrangement of the elsments yet produced; that the table has place for all elements, and fulfils every proper requirement of to-day.

EXPERIMENTS ON THE VAPOUR-PRESSURE OF CONCENTRATED SOLUTIONS OF SEVERAL SALTS, ESPECIALLY LITHIUM AND CALCIUM NITRATES.

By JOHN WADDELL, B.Sc. (Lond.), Ph.D. (Heidelberg), Professor of Chemistry, Royal Military College of Canada.

The experiments, of which those described here are a few, were undertaken at the suggestion of Dr. Goodwin, who had himself sent some reports to the British Association, recording the relative amounts of water-vapour absorbed by sodium and potassium chlorides, when exposed to the same atmosphere, They were begun before the late development of the theory of solutions and the law of vapour-pressure had been enunciated, and a good deal of the work done is not now of much value, and I therefore do not go into the detail that I should otherwise have considered advisable. The majority of experiments on vapour-pressure have, however, been made with very dilute solutions; in these which I describe solutions much nearer the saturation-point were employed.

The method adopted was that to which the name Invaporation was applied, I believe, by Graham, and was carried out in the following manner:—

Into a wide-mouthed closely-stoppered bottle, of about 200 to 300 c.c. capacity, three small test-tubes were introduced, one of which contained water or alcohol, and each of the others one of the salts to be experimented with. After some experience had been gained, the liquid was frequently added directly to the salts, and the third test-tube dispensed with.

The salts first chosen for experiment were calcium and lithium nitrates; nitrates being selected because Dr. Goodwin had worked with two chlorides, and these particular nitrates being chosen because both soluble in alcohol as well as water.

The quantities of salts taken were molecular, weighed in m.grms.; but 1, 2, or 4 mols. of one salt was taken to 1 mol. of the other, so that in some experiments there was a larger amount of calcium nitrate, in others of lithium nitrate. So far as the results recorded here are concerned there was no necessity for this variation, because the numbers retained are all reduced so as to show the quantity of liquid invaporated *per molecule* of the salts. When there was a great excess of one salt, however, and a small amount only of the liquid, it sometimes happened that the latter was entirely absorbed by the salt which was in relatively large quantity; for example, when there were 8 mols. of calcium nitrate to either 2 or 4 mols. of lithium nitrate, and only about 2 decigrms. of water, the latter was all absorbed by the calcium salt, and the result was nearly the same when alcohol was the liquid.

Table of Quantities of Water taken up by 0·164 *grm. of Calcium Nitrate and* 0·069 *grm. of Lithium Nitrate.*

1 $Ca(NO_3)_2$	0·189	0·299	0·367
1 $LiNO_3$ ..	0·142	0·232	0·299

These numbers obtained from experiments in which there were 4 mols. of calcium salt to 1 mol. of the lithium.

1 $Ca(NO_3)_2$	0·125	0·144	0·161	0·241	0·317
1 $Li(NO_3)$..	0·089	0·108	0·124	0·194	0·265

From experiments in which the ratio of calcium to lithium was 2 : 1.

1 $Ca(NO_3)_2$.	0·150	0·221	0·218	0·295	0·423
1 $LiNO_3$ ..	0·105	0·167	0·171	0·230	0·339

From experiments in which the ratio of calcium to lithium was 1 : 4.

1 $Ca(NO_3)_2$	0·137	0·180	0·217	0·264	0·459	0·521
1 $Li(NO_3)$	0·100	0·135	0·172	0·202	0·327	0·403

From experiments in which the ratio of calcium to lithium was 1 : 2.

1 $Ca(NO_3)_2$	0·123	0·129	0·188	0·246	0·248
1 $Li(NO_3)$..	0·044	0·093	0·145	0·196	0·198
1 $Ca(NO_3)_2$	0·365	0·476	0·952	4·228	
1 $LiNO_3$ ..	0·298	0·410	0·819	3·619	

From experiments in which the ratio of calcium to lithium was 1 : 1.

If a curve is plotted whose ordinates are the quantities of water absorbed respectively by the lithium nitrate and the calcium nitrate, it does not differ very much from a straight line, though it is slightly concave towards the axis of the lithium nitrate.

The three cases given in which the amount of water absorbed by the molecular weight of lithium nitrate was less than 0·1 grm. represent what was found to be the general phenomenon, namely, that the calcium nitrate absorbed between 0·120 grm. and 0·130 grm. of water, and had a vapour-pressure equal to that of the saturated solution of lithium nitrate. Hence, while the amount of water absorbed by the calcium nitrate remained practically constant, the quantity absorbed by the lithium nitrate was different in the different experiments, there being more or less of the salt undissolved. After this limit had been passed, the ratio of the water absorbed by the lithium nitrate to that absorbed by the calcium nitrate ranged from about four-fifths to five-sixths.

The formula of lithium nitrate being $LiNO_3$, and of calcium nitrate $Ca(NO_3)_2$, if all the molecules of each were dissociated into their ions there should be the same vapour pressure when the amount of water absorbed per molecule is in the ratio of 2 : 3.

It is therefore plain that the lithium nitrate is dissociated to a greater extent than the calcium nitrate. The ratio of 5 : 6 would be obtained if two-thirds of the lithium nitrate were dissociated and one-half of the calcium nitrate.

In an experiment made with potassium nitrate and calcium nitrate, it was found that 1·932 grms. of water was absorbed by a molecular weight of the former, and 2·836 grms. of water by a molecular weight of the latter. Suppose half of the calcium nitrate to be dissociated, it would follow that one-third of the potassium nitrate is dissociated. If it is known to what extent any one of the three is dissociated, then it would be known to what extent the others are dissociated, but otherwise the ratios give rise to indeterminate equations only.

Experiments were also made with alcohol as the liquid invaporated. There was less uniformity than in the case when water was employed, partly because the alcohol doubtless contained water, as it had not been dried with sodium, but was what had either been bought as absolute or what had been twice distilled over lime. The result may have been partly produced, also, by the fact that it was difficult to make the bottles tight enough to prevent the escape of a little alcohol-vapour. Burnt rubber digested in alcohol was found to be the most satisfactory of the different substances tried for the purpose of keeping the stopper tight.

The numbers given were calculated in the same way as in the preceding case with water. It will be seen that not only does the lithium nitrate absorb more alcohol than it should if the calcium nitrate were equally dissociated, but molecule for molecule an amount absolutely greater. Each molecule of lithium nitrate absorbs approximately four-thirds as much alcohol as each molecule of calcium nitrate. This condition would be fulfilled if all the lithium nitrate were dissociated, and one quarter only of the calcium nitrate molecules.

Table of Quantities of Alcohol taken up by 0·164 grm. of Calcium Nitrate and 0·069 grm. of Lithium Nitrate.

1 $Ca(NO_3)$	0·194	0·312	0·408	0·612
1 $LiNO_3$ ..	0·324	0·427	0·575	0·889

From experiments in which the ratio of calcium to lithium was 4 : 1.

1 $Ca(NO_3)_2$	0·178	0·256	0·341	0·474	0·618	0·935
1 $LiNO_3$ ..	0·220	0·332	0·460	0·696	0·896	1·388

From experiments in which the ratio of calcium to lithium was 2 : 1.

1 $Ca(NO_3)_2$	0·224	0·266	0·372	0·600	1·236
1 $LiNO_3$ ..	0·280	0·331	0·469	0·845	1·552

From experiments in which the ratio of calcium to lithium was 1 : 2.

1 $Ca(NO_3)_2$	0·204	0·283	0·360	0·533
1 $LiNO_3$ ..	0·244	0·368	0·480	0·726

From experiments in which the ratio of calcium to lithium was 1 : 4.

1 $Ca(NO_3)_2$	0·482	0·718
1 $LiNO_3$ ..	0·657	0·987

From experiments in which the ratio of calcium to lithium was 1 : 1.

In order to compare the members of the calcium group of metals among themselves and with lithium nitrate, a series of experiments was instituted. Barium and strontium nitrates being less soluble than calcium nitrate, a larger quantity of water was needed than for the calcium and lithium salts, and within the limits in which I have hitherto worked the results are not very concordant; but I give the numbers without delaying the paper for the further investigations which I propose making, and which will take some time. There seems to be little doubt, from what has been done, that the barium nitrate is the most absorbent; that the calcium salt comes next; and that the strontium compound, instead of being intermediate between the others, is less absorbent than either.

Table of Quantities of Water absorbed by each Molecular Weight expressed in Milligrammes.

1 $LiNO_3$ ...	—	—	0·460	1·182	—
1 $Ca(NO_3)_2$	0·590	1·166	—	—	0·797
1 $Sr(NO_3)_2$	0·504	1·115	0·470	1·320	0·685
1 $Ba(NO_3)_2$	—	—	—	—	—

1 $LiNO_3$ ..	0·327	0·761	—	1·339
1 $Ca(NO_3)_2$	—	—	8·205	[1·607]
1 $Sr(NO_3)_2$	0·331	0·830	—	[1·495]
1 $Ba(NO_3)_2$	—	—	8·994	1·671

The relationship spoken of above will be seen in the last column. The unbracketed numbers are the result of direct experiment; of the bracketed numbers that for calcium nitrate is obtained by calculating the water absorbed by that salt as six-fifths the amount absorbed by lithium nitrate, and that for strontium nitrate is deduced from the figures in the fourth column, where it will be seen that strontium nitrate absorbs 1·320 grms. of water for 1·182 grms. absorbed by lithium nitrate.

Finally, a series of experiments was made in which the metal was the same, but the salt radical varied. The haloid salts of potassium were chosen for experiment. It appears that these salts are very nearly equally dissociated, even in rather concentrated solutions, but if anything the bromide is more dissociated than the others.

Table of Quantities of Water taken up by the Milligramme Molecular Weight of Potassium Chloride, Bromide, and Iodide.

1 KCl	0·060	353	553	126	506	797
1 KBr	0·229	377	588	—	—	—
1 KI	0·229	373	581	229	522	797

1 KCl*	2·070	0·088	0·312	747	2·237
1 KBr	—	0·229	0·326	784	2·339
1 KI*	1·933	0·229	0·328	802	2·310

1 KCl	0·595	295	248	411	605	1·190
1 KBr	0·606	311	251	—	—	—
1 KI	—	—	—	428	624	1·205

1 KCl	200	407	1·027	266	690	376
1 KBr	—	—	—	296	—	396
1 KI	226	431	1·057	—	—	—

1 KCl	781	401	781	769	188	560	238
1 KBr	827	—	—	—	—	—	252
1 KI	—	415	789	775	233	589	—

(Note.—The numbers marked with the asterisk are peculiar, as in no other case does the KCl absorb more water than the KI. In this instance more water had been added originally to the chloride than to the iodide, and invaporation does not seem to have been complete even after a lapse of two years. It turned out that some water-vapour escaped from the bottle, for a weighing made since this paper was written, and six months after the one recorded above, gave KCl 2·033 and KI 1·931. Thus the main loss was from the chloride, and I have no doubt that now that the stopper has been made tight the anomaly will disappear.

When the quantity of water to be divided among the salts was small, a phenomenon, similar to that observed with the lithium and calcium nitrate, is again prominent. The bromide and iodide absorbed the water, the chloride apparently being left dry until the other salts had absorbed a considerable quantity of water.

In two cases the bromide and iodide have 229 m.grms. of water each, while the amount of water with the chloride is in one case 60 m.grms. and in another 88 m.grms. In another experiment the same number 229 is found for the iodide, while the chloride has 126. Still another experiment gives 226 with the iodide and 200 with the chloride. We may therefore conclude that the bromide and iodide would probably absorb a constant amount of water whenever the quantity is more than 450 m.grms. and less than a little over 650 m.grms., snd that the chloride absorbs what is left over.

So soon as this limit is passed, the three salts absorb nearly the same amounts of water, as shown by the case in which the bromide absorbed 257 m.grms. and the chloride 248 m.grms. It appears, then, that the bromide and iodide of potassium both absorb enough water to make a solution, while the chloride is still in the solid condition, and when the vapour-pressure from the bromide and iodide comes to be as large as that of the saturated solution of the chloride it remains constant until the chloride is all dissolved.

The peculiarity of the lithium nitrate, as compared with calcium nitrate, is the most noticeable feature in the experiments, and I have therefore begun some experiments with chlorides and sulphates, which, however, will require time for completion. Meantime I made a rough set of experiments, on the electrical resistance of strong and dilute solutions of lithium and calcium nitrates.

6·9 grms. of lithium nitrate were dissolved in 100 grms. of water, and to 10·277 grms. of this solution 349 grms. of water were added.

In the same way, a strong and a dilute solution of calcium nitrate was made. 8·2 grms. of calcium nitrate were dissolved in 100 grms. of water, and to 10·377 grms. of this solution 352·4 grms. of water were added.

The resistance of these liquids was determined in the following manner:—

The vessel containing the solution was put in circuit, with Lord Kelvin's composite balance and his set of anti-inductive resistance-coils. An alternating current, such as used for incandescent lighting purposes, was employed, and its electromotive force was determined by a statical voltmeter. The current was read directly from the balance, the difference of potential was given by the voltmeter, and therefore the resistance could be calculated. Since the resistance in the box was known, the resistance of the solution could be calculated by subtracting it from the total resistance. The vessel in which the liquid was contained, whose resistance was measured, was a U-tube of about 30 c.c. capacity. The electrodes were kept at the same distance, in the different experiments, by resting on the ledges produced by the narrowing of the tube at the bend.

The average resistance of the strong solution of calcium nitrate was 238 ohms. The average resistance of the dilute solution was 3690 ohms. In the case of the lithium nitrate the resistance of the strong solution was 167 ohms, and of the dilute solution 4114 ohms. If the salts had been equally dissociated in the strong and dilute solutions, and if the current is carried only by the dissociated ions, the resistance of the dilute solutions of the calcium nitrate should have been 8100 ohms, and of the lithium nitrate 5827 ohms. The resistance of the calcium nitrate actually increases in a much less ratio than the dilution, while the lithium nitrate does not show so great a divergence.

The amount of dissociation of the calcium nitrate is about 45 per cent as great in the strong solution as in the weak, while the amount of dissociation in the case of the lithium salt is about 83 per cent.

Owing to several sources of error, such as the fluctuation of the electromotive force of the circuit, and the difficulty of taking accurate readings, when the current was small, the results attained do not pretend to close exactness; but they show the nature of the change produced by dilution, and that in the strong solution calcium nitrate is much less dissociated than lithium nitrate. Moreover, the result obtained for the latter salt does not differ very greatly from that given for lithium chloride in Ostwald's "Outlines of General Chemistry" (English edition, p. 261).

Nearly all of the experiments in invaporation recorded above were with solutions more concentrated than even the nearly normal solutions, which were the strongest employed for the determination of electrical resistance.

It was stated that the ratio obtained between the quantities of water absorbed by the two salts, when the vapour-pressure was the same, would be satisfied if two-thirds of the lithium nitrate were dissociated and one-half of the calcium nitrate.

The table given by Ostwald shows that in the normal solution of lithium *chloride* the dissociation is about 61 per cent, and my experiments on the electrical resistance seem to show that lithium nitrate is somewhat similar to the chloride. Very probably, then, this calculation is not very far astray.

I should perhaps add that the bottles containing the tubes with which the invaporation experiments were made were at the temperature of the laboratory, which varied between 10° C. and 25° C. at different times of the year. I have weighed the same tube, however, in spring and autumn, and the weight was within a m.grm or two the same, so that the variations of temperature had no appreciable effect.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 190).

So long as a spectroscopic examination enables one to detect the presence of sodium in a flame burning in air, either *at rest* or *in motion*, this air imparts to platinum, in whatever state it may be, the property of colouring the flame yellow. Spongy platinum possesses this property in a marked degree.

The time necessary for the deposit of sodium on platinum is very variable; with the ordinary air of the *laboratory* from ten to fifteen minutes are sufficient, whilst several days' exposure are necessary for producing the yellow colour in the flame when the air only shows slight traces of sodium.

Even spongy platinum, when kept lying in a glazed cupboard in dry air, in which spectrum analysis is unable to detect the presence of sodium, only acquires the property of turning a flame yellow after several days' exposure; but a spectrum analysis of the flame *before it has changed colour* shows a faint image of the sodium D line.

It follows from these experiments that it is always the air which deposits sodium on platinum.

Silver behaves like platinum. When properly refined, as I have described, it shows no trace of the sodium spectrum. After having been left in air in which spectrum analysis shows a bright yellow sodium line, it imparts a distinctly yellow tint to a Bunsen burner flame, and shows a strong sodium line. This colour quickly disappears; but if the metal be covered with atmospheric dust it colours the flame yellow, and this property remains until it has been melted and properly refined in a lime crucible.

The tubes and silver fittings, when kept in air, should be carefully washed with water mixed first with hydrofluoric acid, then with hydrochloric acid, and afterwards with pure water.

Bone-black when refined behaves exactly like platinum and silver. It attracts the deposit of sodium. It should be kept in *air-tight jars*, and should never be used until after having been raised to white heat.

Platinum, silver, and carbon, when kept *protected from atmospheric dust* in cupboards, well-closed glass cases, under bell-jars, &c., acquire a deposit of sodium on their surfaces. The sodium is evidently contained in the outside air which continuously mixes by *diffusion* with the air inside the cupboards, cases, and jars. The rapid deliquescence of highly soluble compounds, when left in these confined spaces, is evidence of the rapid rate of diffusion. This fact, moreover, is known to everybody who puts drying agents into cases, however air-tight they may be, to preserve instruments or chemical compounds from the action of water vapour in air.

Experience has taught me that *one must moisten the inner surface of the tubes and metal or rubber fittings used to bring the gas from the reservoir to the apparatus, and never to use rubber tubes desulphuretted by placing them in a boiling solution of dilute hydro-oxide of sodium.* When undertaking this desulphuretting one day I lost time in looking for the reason of the presence of a great deal of sodium. The soda penetrates into the rubber; the illuminating gas, by attacking it, charges itself with sodium when passing through a rubber tube desulphuretted with hydrate of sodium, even although the tube has been washed with water containing a little acid and then dried.

It was by pondering over the above facts and conclusions that I sought to solve the problem of ascertaining if it be possible to obtain metals and metallic compounds, which, at the highest temperature attainable, should not show the characteristic spectrum of sodium on spectroscopic examination, and whether one could thus change the spectrum of metals the one to another, or at least produce the characteristic rays of the spectrum of one metal by using a compound of another metal.

Having described my researches on the spectra of the metals on which the experiments were conducted, I must describe the method used to vapourise them and the instruments I used.

On the Methods of Volatilising Metals and their Compounds.

I have used, one after the other, all known methods for attaining this end: they consist of the introduction of the bodies into—

1. The outer envelope of the Bunsen burner flame.
2. The outer envelope of a pure hydrogen flame issuing from a platinum blowpipe.
3. A blowpipe jet of pure hydrogen and pure air.
4. A jet of pure hydrogen raised to incandescence by the admixture of oxygen.
5. A jet of coal-gas rendered colourless by the admixture of oxygen.
6. The internal cone of an oxyhydrogen blowpipe.
7. The internal cone of an oxy-coal-gas blowpipe.
8. An induction-spark from 2 to 5 m.m. between the points, with or without condensers capable of giving respectively sparks of 5, 15, and 45 c.m. length, the substance being either solid, or melted, or in solution in pure or acidulated water, and either in air or hydrogen.
9. A discharge from 5 to 10 m.m. between the points, capable of giving sparks from 15 to 45 c.m. long, having from *one* to *five* very large Leyden jars intercalated, the substance being either solid or dissolved in acidulated water, and either in air or hydrogen.
10. An electric arc formed successively between pure carbon electrodes: 1st, by 30, 50, 100, or 200, of the very largest Bunsen cells; 2nd, by a battery of 33 Julien accumulators, giving at the terminals of the lamp 10 ampères and 30 volts, and forming an arc 9 m.m. long by about 8 m.m. diameter; 3rd, by a Gramme and Siemens dynamo coupled, giving at the terminals of the lamp from 28 to 30 ampères and from 60 to 80 volts, and forming an arc $2\frac{1}{2}$ c.m. long by about 8 m.m. diameter; 4th, by a 10,000 candle power dynamo.*

These methods having been previously used, and their applications being known, I can limit my description to pointing out some facts that long practice has taught me.

On the Position to be given to Flames when Examining their Spectra.

Messrs. Bunsen and Kirchhoff recommend placing the dark part of an ordinary gas flame or a hydrogen flame in front of the slit in the collimator, and putting the platinum wire loop, or coil, with the compound to be vapourised, in the middle of the outer envelope of the flames on the side opposite the slit.

It is a well-known fact that, with a minute quantity of incandescent vapour, we can produce spectra which leave nothing to be desired on the score of distinctness, when the light thus obtained is sufficiently intense; but this condition can only be realised when working with very volatile bodies. It is not the same with less volatile compounds. In this case it seems better to set the jets beside the collimator so that the *right* or *left* edge of the flames is exactly opposite the slit with the centre of the edge in the axis of the collimator. By arranging it thus, one gets all the rays proceeding from a compound vapourised in the middle of the outer envelope of the flames. To satisfy oneself that this arrangement intensifies the light, it is sufficient to compare the spectrum of chloride of barium in both positions in the same flame, whether Bunsen burner or hydrogen. I am aware that under these conditions the rays have not all the same focus; but the same inconvenience is found in the usual method, because, when introducing the substance to be volatilised, one almost always pierces through the dark envelope and penetrates too far into the flame. I am willing to admit that the method I have adopted is less convenient than the one generally used, and that it requires practice to do it quickly. The difficulty of doing it is a good guarantee for the accuracy of the result. It is, in fact, necessary to place the flame so that the centre of its dark envelope is exactly on the axis of the collimator; this necessitates the absolute immobility of the flame—an immobility hard to obtain in a room where the air is more or less in motion, but still it may be obtained by using screens to shield the flame from air-currents, or, better still, by maintaining a constant pressure of from 2 to 4 c.m. of water by means of a hydrogen and air or coal-gas and air blowpipe, with a burner ending in a platinum nozzle with a hole from $\frac{1}{2}$ to 1 m.m. in diameter. With the flame in this position, using a sufficiently narrow slit, one avoids, as far as possible, oblique rays, and the background of the spectrum is always dark, whether there be lines or no. By the usual method a continuous spectrum appears so often that all spectroscopists imagine potassium and sodium to have a continuous spectrum, although I have proved that the parts in the neighbourhood of the sodium D line or potassium lines are completely free from luminosity, even although the potassium and sodium compounds be put into almost incandescent hydrogen, such as an oxyhydrogen blowpipe fed with a proper quantity of oxygen. The easiest method of adjusting the flames is as follows:—On one side I arrange on a board, on the table of a strong camera-stand used to carry the spectroscope, the Bunsen burner, and the hydrogen, hydrogen and air, oxyhydrogen, or oxy-coal-gas blowpipe, surrounded by screens to protect them against lateral air-currents. This board, the length of which is nearly half the width of the table, moves by means of an endless screw at right angles to the axis of the collimator of the spectroscope. To effect this the worm works in an easily turned screw, which is fixed by its collar in a bearing on the *left side* of the table.

On the other side, on a second board, which occupies the right half of the table, I arrange the holder used in putting the compounds into the outer envelope of the flames. The second board also moves at right angles to the axis of the collimator, by means of an endless screw attachment on the *right side* of the table.

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* In the descriptions of the luminous spectra of sodium, lithium, calcium, strontium, barium, and thallium, I give details of the use made of the arcs from different batteries and dynamos

By this means the endless screw attached to the board on the *left* causes the burner or blowpipe on it to advance or recede from *left* to *right*, whilst that on the right causes the holder on the other board to move forward or back from *right* to *left*.

As the pitch of the screw is very fine, *a millimetre at the outside*, one can bring the rays from the incandescent vapour under spectroscopic examination into the axis of the collimator of the spectroscope with great accuracy.

This arrangement enables the observer to move either the flame or the holder without removing his eye from the eyepiece of the spectroscope; this is necessary when he only has small quantities of matter to deal with, because he can work alone without injuring the relative purity of the air, and at the same time avoid any error following the appearance of a line caused by disturbing the flame.

Experience has taught me that in order to completely avoid a continuous spectrum, one must eliminate rays from the incandescent holder. These rays extend farther than is generally thought. In many cases they extend more than 2 c.m. along the holder. One effects this by putting the compound into the flame at least *two centimetres* from the edge of the slit through which the rays pass, and by arranging in front of the slit in the collimator movable platinum diaphragms which can be opened or closed at will, according to the height of the luminous beam required to pass the slit. Many spectroscopes actually have an attachment for this purpose, especially the large instruments made by M. Hilger.

I have already described the Bunsen burner as much as is necessary, so I need say nothing further about it.

On the Blowpipe.—As for the apparatus used for producing the hydrogen jet, or the hydrogen and air, oxy-hydrogen, coal-gas and air, or oxy-coal-gas blowpipe, it consists of a tube of platinum, silver, or copper, according to circumstances, bent near its free end to a right angle, ending in a nozzle of platinum, silver, or pure gold. The bore of the nozzle is from ½ to 1 m.m. diameter, according to the length of flame I want to obtain with a constant pressure of 2 or 4 c.m. of water, measured by a manometer inserted between the blowpipe and the gasometers. I use a platinum nozzle, with an opening $\frac{2}{10}$ m.m. wide and 1 c.m. long, when I want a simple sheet of burning hydrogen. Before being adjusted to the bent tube, the nozzles are always washed with dilute hydrofluoric and hydrochloric acids, then with pure water, and finally heated to redness.

To guard against explosions, I use as a blowpipe ther well-known apparatus employed by Mr. G. Matthey fo fusing platinum. The mixture of gases used in it may be varied at will, by the taps fitted to it.

I think I ought to mention that it is necessary to wash and keep moistened with pure water the inside of the blowpipe, so as to prevent the presence of, and consequently avoid detaching, adherent sodium dust. The terminal tube of the blowpipe is held in a vice working on a rack on a vertical stand. The arrangements are such that I can have at will, at a pre-arranged height, a vertical, horizontal, or sloping jet, according to the conditions I have to satisfy.

In the note on the thallium line in the flame and electric spectrum, I fully explain the use of the hydrogen and air and coal-gas and air blowpipe flame.

(To be continued).

A New Black Ink.—Mr. G. Vickers, of Angel Court, Strand, is introducing a new blue-black non-corrosive ink having properties that should recommend it to the writing public. It is very fluid and dries a fine black, works well with ordinary steel pens, and does not go sticky; it will therefore be useful for stylographic pens, &c. Acids appear to have less effect upon it than upon many of the aniline inks now on the market.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending September 30th, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 10th, 1895.

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 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 Sept. 1st to Sept. 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 175 samples examined all were found to be clear, bright, and well filtered.

The weather during September has been in every respect remarkable, the rainfall in the Thames valley having dropped from 2·66 inches (the average of 25 years), to 0·57 inch, leaving a deficiency of 2·09 inches. Rain fell on six days only, the bulk of it, 0·39 inch, on Sept. 6th.

This, together with the excess of sunlight, has had a marked effect on the quality of the water, as can be seen by the following table:—

Comparison of the Averages of the Five Thames-derived Supplies for the Months of August and September, 1895.

	Common Salt. Per gall.	Nitric Acid. Per gall.	Hardness. Degrees.	Oxygen. reqd. Per gall.	Organic Carbon. Per gall.	Organic Carbon. Per gall.	Colour. Br'n : Blue
	Means.	Means.	Means.	Means.	Means.	Max.	Means.
Aug.	1·994	0·740	13·09	0·039	0·093	0·108	11·7 : 20
Sep.	1·980	0·685	12·97	0·032	0·081	0·098	10·4 : 20

Bacteriological examinations of the filtered and unfiltered samples have been carried on unremittedly throughout the month, and we find that the average of raw unfiltered Thames water contained 2432 microbes per cubic centimetre, and river Lea water 1710 microbes per cubic centimetre; whereas the filtered samples from the five Thames Companies contained only 62 microbes per cubic centimetre, and the filtered Lea water 73 microbes per cubic centimetre.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

Researches on the Essence of Bergamot and on its Sophistications.—Dr. Ignazio Campolo.—This essence is an oily mobile liquid of a dark yellow colour, an acrid and pungent taste, and a peculiar, delightful, and penetrating odour. It has a slightly acid reaction, and a specific gravity at 15° of 0·887. Like the other essences of the Aurantiaceæ it is optically active, deflecting the plane of polarised light to the right. The principal sophisticants to which essence of bergamot is liable are fatty oils and resin. The weight of residue left by the genuine essence on evaporation does not exceed 6 per cent. The increase of the weight in sophisticated samples is equal to the quantity of olive oil added.

DETERMINATION OF URANIUM IN ORES CONTAINING PHOSPHORIC AND ARSENIC ACIDS.

By R. FRESENIUS and E. HINTZ.

In the determination of uranium in ores containing phosphoric and arsenic acids, copper, and iron, by means of ordinary methods various difficulties were encountered. In the first place, the precipitate consisted chiefly of arsenic and copper sulphides, and sulphur could only be obtained free from uranium after repeated precipitations by hydrogen sulphide in an acid solution. Secondly, the presence of phosphoric acid greatly increases the difficulty of separating iron from uranium.

A method was therefore sought for of precipitating uranium from an acid solution, in order thus to effect the separation of phosphoric and arsenic acid. For this purpose precipitation with potassium ferrocyanide seemed a suitable means. But if the precipitation of the uranium is effected in the ordinary manner, the result is that the precipitate of uranium ferrocyanide scarcely subsides and cannot be filtered off. But if, after the addition of the potassium ferrocyanide, the liquid is saturated with sodium chloride, the precipitate quickly subsides, and can be easily filtered and washed with water containing sodium chloride.

On the basis of these facts, the determination of uranium in ores containing the above-mentioned ingredients can be executed as follows without difficulty:—

We first separate as usual the silica from the solution in nitric or hydrochloric acid or aqua regia, add an excess of potassium ferrocyanide to the slightly hydrochloric solution, and saturate the liquid with sodium chloride. The precipitate, which subsides quickly, and contains uranium-, copper-, and iron-ferrocyanides, is first washed by decantation, and afterwards on the filter completely with water containing sodium chloride, and is then treated in the cold with dilute potassa-lye. After the transformation of the ferrocyanides is completed and the hydroxides have deposited, the liquid is poured off through a filter, washed once more by decantation with water, rinsed on to a filter with a little water containing ammonium chloride and ammonia, and washed with the same liquid without interruption until potassium ferrocyanide can no longer be recognised in the filtrate after acidulation.

The hydroxides are then treated with hydrochloric acid, in which they dissolve completely if the above-mentioned operations have been correctly carried out. If there remains an insoluble residue of ferrocyanide it must be washed and again treated with potassa-lye, as above directed.

The solution of the metallic chlorides which no longer contain phosphoric or arsenic acid, if the precipitated ferrocyanides have been well washed, is concentrated if necessary, the greater part of the free acid is neutralised with ammonia; the liquid (still clear) is mixed with ammonium carbonate in moderate excess, allowed to stand for some time; the ferric hydroxide which remains undissolved is filtered off, washed with water containing a little of the filtrate with the addition of the washings, heated in order to expel the chief part of the ammonium carbonate, acidified with hydrochloric acid—whereby the yellowish flocculent precipitate formed on boiling, and containing a part of the uranium, is re-dissolved—and the copper remaining in the solution is precipitated with sulphuretted hydrogen with the application of heat. The copper sulphide was always obtained free from uranium. The liquid filtered from the former is concentrated, the uranium precipitated with ammonia, and the precipitate of uranium hydroxide is converted into uranic-uranous oxide by ignition in an uncovered crucible, and weighed as such. As a check-experiment, it is then converted into uranous oxide by ignition in a current of hydrogen, and the weight is again determined.—*Zeitschrift für Analytische Chemie*, xxxiv., p. 437.

NOTICES OF BOOKS.

Kurzes Handbuch der Kohlenhydrate. (II. Band). By B. Tollens. Breslau: E. Trewendt. 1895.

Modern chemistry is like modern music in acknowledging more and more the sway of the *leit-motif.* Reading the history of the science backwards, it is always easy to give a "too, too solid form" to that which is only a ghostly presence; in other words, to discover the dominant theory of a period long before it existed. But in dealing with *the* forward movement of our own present time, the ordering and systematising of the group of carbohydrates, there is no doubt that the results in this case are begotten of the theory. Nor could there be any better exemplification of the character of the movement than a careful comparison of the volume before us with its predecessor (I. Band, 1888), of which it is a substantial amplification, and in some respects a revision. The *leit-motif*, it is hardly necessary to premise, is the theory of the asymmetrical satisfaction of the four combining positions of the C-atom; this, as the basis of the "new isomerism," which specially characterises the carbohydrates.

Nor is it necessary to make more than a passing allusion to the "Seer" of the movement. Emil Fischer's position in relation to the subject-matter of the book is duly recognised in the author's preface. His work as a pioneer investigator has about it, we may remark, much that is unique. For while it has undoubtedly carried with it a number of discoveries of compounds and methods, with perhaps the attendant stimulus of novelty, its main purpose was the laborious verification of a strictly mathematical or geometrical forecast. Such "high academical" work is rare in our science, and it has a moral aspect which ought to give pause to those who talk lightly of "*fin de siècle* evolution."

We may contrast the "sugar movement" with the great development which preceded it—the chemistry of the aromatic series. This involved the elaboration of an equally striking chapter in isomerism, but the principles were in this case evolved *a posteriori.* The "inwardness" of this movement, moreover, centred in large measure round the peculiar, but extrinsic, attractiveness of the particular compounds which were brought to light with a prolific fertility. No one so far as suggested any striking development of art or industry as likely to follow from the discovery of the thirteenth hexanpentolal. Still, the melancholy conclusion that "there may be no money in it after all"—a finally destructive argument in many spheres of activity—would have had no more deterrent effect upon the pursuit of this particular No. 13 than it has had in damping the ardour of North Pole enthusiasts.

But, to the book. The author needs no introduction to English chemists. His researches in special chapters of the now great volume of carbohydrate chemistry are well known; and his contribution of experimental methods has been especially valuable. No one will question his qualifications for the task of chronicler of the movement in which he has taken so active a part, and, with the two monographs which he has produced before us, we are justified in saying the work could not have been in better hands. A preliminary idea of the scope and magnitude of the present volume (Part II.) will be gathered from the fact that there are over 1200 references to original papers. The systematic arrangement of the subject-matter is necessarily based upon the classic work of Fischer, of which the Maestro himself has given a comprehensive digest in his papers entitled "Synthesen in der Zuckergruppe" (*Berl. Ber.*, 1890, p. 2114; 1894, p. 3189), The general relationships of the group, as disclosed by systematic synthesis and dissection (Abbau), the broader questions of constitution, and the more refined conclusions as to configuration, are dealt with in a preliminary section, which also includes a general account of the more special characteristics of the group, *e.g.*, optical properties, thermal constants, fermentation, and other hydrolyses. This section is admirably condensed into 55 pages of the text. Candidates for competitive examinations will rejoice in the prospect hereby afforded of "getting up" this great subject in the compass of, say, one evening!

The table of genealogical descent of the typical hexoses, *d*-glucose and *d*-fructose, from formaldehyd, acrolein bromide, and glycerin, will appeal with force to the "cram" school of students. In the more serious view, it affords an excellent perspective of a whole campaign of methodical struggle. We will not, however, discuss the author's preamble according to its "location," but, to follow an excellent precedent, after the encyclopædic portions of the work have been noticed. In dealing with this, the experimental subject-matter, the author follows the received order:—(*a*) The carbohydrates proper (aldoses and ketoses) are dealt with as mono-, di-, and tri-saccharides, *i.e.*, generally the crystallisable sugars, in order of molecular weight, and lastly, the poly-saccharides; (*b*) the mannites or mannitols, or corresponding alcohols; (*c*) derivatives of the cyclic hexamethylene (inosite, quercite, &c.); and lastly, (*d*) the diversified group of saturated poly-hydroxy-acids derived from, or constitutionally related to, the carbohydrates.

There is little to be said in criticism of these sections. It is difficult to see how the work could have been more carefully done. To have selected the subject-matter from over 1200 original papers, and reproduced their essential features in 300 pages of text, is an invaluable effort of digestion and concentration. Specialists will possess themselves of the book at once, as a matter of course, and their judgment of its value will not be influenced by "these presents"; nor would its value as a work of reference be materially lessened by any objections on points of detail. Those who are not specialists can afford to believe in a few substances of doubtful identity, and accept some conclusions which they may have to unlearn, without prejudice to the advantage of taking a categorical survey of a careful census of this well-marked province of chemical individuals.

Thus, on the doubtful side. Some of the conclusions as to the identity of isomaltose will, in view of Brown and Morris's recent work, require revision. The author's view of the molecular structure of cellulose may be summed up as that of an "acetal" union of unit C_6-groups, against which there appears to be a good deal of experimental evidence. This particular section, which includes the ligno-celluloses, has an amorphous character. But so have the compounds themselves, and hence the "Cinderella" position they continue to enjoy. If we wished to be oracular, we should prophesy concerning this group of out-casts *and* the Twentieth Century.

It is evident that no useful purpose would be served by an examination in detail of the encyclopædic matter of the text. It is of necessity a compilation: no pains have been spared in the collection and ordering of the experimental material, and considering the difficulty of photographing an expanding group—if we may be allowed the simile—the author is very much to be congratulated on the result.

What is perhaps of greater moment is the general plan of the work as sketched in the preamble, which is, or aims to be, co-extensive with the present development of the subject. This we think is somewhat too narrow; possibly the author has circumscribed it with intention. Those who follow the literature of the subject are aware that it is overflowing in every direction into the province of the physiologist. In fact, the sugar chemist is *ex officio* a physiologist. Fischer himself having laid his structural foundations on the most purely academic lines, now finds unexpected relationships of configuration to both the constructive processes of assimilation and the destructive processes of hydrolysis and ferment re-solutions. Brown and Morris, in this country, have contributed a memoir of fundamental import upon the root problems of assimilation. Tollens, also, and his students past and present, are doing valuable work in physiological problems.

Of course the inevitable consequence of exhaustive investigation of the carbohydrates is to open out the whole province of plant chemistry. But there are further consequences in view. The whole science of carbon chemistry is becoming involved. We have had a century of "pure chemistry." We have learned to treat matter as matter, with a respect which our mediæval ancestors failed even to anticipate. At this date we take Matter very much for granted (writing it with a capital M), and find our fascinations in problems of form. So far as these are purely geometrical they tend to finalities. Of course we could go on multiplying analogues to the end of time. But there enters the question of brain or mind exhaustion, and the antidote of new objectives. The new objective of organic chemistry is the chemistry of living organisms. We see its operation in all hands; there is no need to enforce the conclusion by demonstration. At the same time we do not feel "superfluous" in calling attention to this general convergence or divergence of research in connection with the subject of the book before us. As we have indicated, the author is sparing in his treatment of the physiological relationships of the subject-matter. The suggestive conclusions of Fischer, as to the relationships of assimilation and ferment resolutions to the configuration of the assimilating substance or ferment, are very sparingly noticed. There is no mention of the observations of A. J. Brown on the cellulose-forming properties of *Bacterium xylinum*. There are no special references to that most interesting problem presented by the natural history of the carbohydrates, viz., the passage from saturated to unsaturated compounds. On the other hand, a glance at the Index will show that particular references to plant products are extremely numerous, and, as a knowledge of the author's researches, leaves us in no doubt as to his being a great student and patient investigator of the chemical problems of plant-physiology, we must conclude either that the plan of the work is not to admit of the discussion of physiological problems which is perhaps conveyed by the title, or that the task of dealing with these is deferred to a third volume.

If, therefore, the work in its present state of development leaves us with this one impression of shortcoming, it may be the result of a little *trop de zèle* on our part. Still we can all of us afford to be a little over-zealous when not engaged in putting ourselves "on record"; and it will be well if our teachers will put all their spare enthusiasm into a definite shaping of the careers of promising students towards the new fields of investigations now opening up.

Prof. Tollens's work is perhaps too strictly academical to be directly suggestive of fruitful subjects of research. But with the interpretations and forecast of the teacher it cannot fail to exert a most valuable influence in furthering the progress of the newest "New Chemistry," which is the chemistry of the plant cell.

Justus von Liebig: His Life and Work (1803 to 1873). By W. A. Shenstone, F.I.C., Lecturer on Chemistry in Clifton College. Small 8vo., pp. 220. London, Paris, and Melbourne: Cassell and Co., Limited. 1895.

Mr. Shenstone is right. Though not a quarter of a century has elapsed since Justus von Liebig joined the majority, and great as had been his services to Science and to the most useful of all the Arts, he is, save in scientific and technical circles, nearly forgotten. Our author mentions two instances showing how little he is known even among the "educated and respectable" classes. One current notion is, that Liebig was a man who gained a large fortune by making "extract of meat." Others think they have heard his name mentioned in connection with agriculture. A very common mistake is the notion that Liebig's father was a pharmacist, and that the great luminary of Giessen and Munich himself was brought up to the same career. He had certainly been placed for a short time with an "apothecary," or, as he would be termed in England, a "chemist and druggist;" but after ten months his non-pharmaceutical experiments proved so alarming that his master was glad to get rid of him.

The work before us deals not so much with Liebig's private life as with his career and his influence upon Germany and upon the world. But there is one point to which attention cannot be too forcibly and too frequently drawn. In the earlier part of the century in Germany—as it is still to a deplorable extent in Britain—the mental calibre of a youth was judged solely by his power of assimilating the "classics," of remembering long strings of rules and exceptions, and of playing with "longs and shorts." Liebig had little verbal memory, and no taste for word-mongering. Hence he was denounced as a dunce, likely to be a disgrace to his teachers and his parents. What an instructive mistake! The classical scholars who were considered so greatly his superiors have passed, leaving the world no wiser than they found it, whilst Liebig has bequeathed to future generations a solid inheritance of research which is still continuing to grow and to bear fruit.

After an Introduction, and an account of his friendship for Woehler and of their joint researches, the author goes on to describe Liebig's discoveries in pure chemistry, his relations with Dumas,—which were not uniformly harmonious,—his acceptance of the fruitful doctrine of substitution, his researches on fermentation—involving a dispute with Pasteur, of which Mr. Shenstone speaks perhaps too favourably. We have then his epoch-making contributions to the chemistry of agriculture and to physiological chemistry.

A special chapter is worthily devoted to his educational work. To him, more perhaps than to any other man, is due the splendid upburst of intellectual life which has made the German universities foci of discovery, and has even contributed powerfully to the development of German manufacturing industry. It has been said that the first Napoleon was able to "spit" generals. In like manner it may be said that Liebig could "spit" discoverers, inventors, professors, full of originality and carrying on the work of their great master.

Liebig's "Familiar Letters on Chemistry" are not overlooked. It is very truly said that these letters "had much to do with the present intelligent attitude of the German 'practical man' towards Science, which has contrasted so strangely with that of his average English brother for many years past, much, it is to be feared, to the material disadvantage of the latter." The German has learnt that, to ensure manufacturing superiority, abundant capital, business tact, and energy are not sufficient without a knowledge of the scientific principles on which the various industrial arts are based.

Mr. Shenstone deserves hearty thanks for the production of a work so opportune and so useful.

A Short Manual af Analytical Chemistry, Qualitative and Quantitative, Inorganic and Organic: following the Course of Instruction given in the South London School of Pharmacy. By John Muter, Ph.D., F.R.S.E., F.I.C., &c.; Analyst to the Metropolitan Asylum Board; Public Analyst for Lambeth, Wandsworth, Southwark, Newington, Rotherhithe, and the Lindsey Division of Lincolnshire; Past President of the Society of Public Analysts; late Editor of the *Analyst*. Sixth Edition, Illustrated. London: Simpkin, Marshall, Hamilton, Kent, and Co. (Limited); and Baillière, Tindall, and Cox. 1895.

The work before us, though primarily intended for the guidance of pharmaceutical students, will be found widely useful. Setting out with a view of the processes employed by practical chemists, the author proceeds to the detection of the metals in which cerium is included, though indium, rhodium, thallium, and uranium are omitted, doubtless as not being used in medicine.

Next follow methods for the detection and separation of the acid radicles, the qualitative analysis of mixtures of unknown salts, the qualitative detection of alkaloids of some other organic substances used in medicine, and a general sketch of procedure in toxicology.

Successive chapters treat of weighing, measuring, and specific gravity, no notice being taken of the very useless hydrometer of Beaumé. Next follow instructions for volumetry and the use of the nitrometer, the gravimetric determination of metals and acids, for the determination of phosphates in soils and manures, and for the full analysis of the organic matters in potable waters. Instructions are given in ultimate organic analysis, the nitrogen being determined according to the processes of Dumas, of Varrentrapp, and of Kjeldahl.

In Chapter X. there are given special processes for the sanitary examination of waters, of air, and of the more usual articles of food. Referring to Pepper, we cannot help asking why the importation of "poivrette" is still permitted? Special processes are laid down for the analysis of the more important drugs, of urine, and urinary calculi.

In the concluding chapter there are instructions, necessarily rather brief, for gas analysis—now of rapidly increasing importance—and of polariscopic and spectroscopic analysis. The section on the analysis of urine is enriched with illustrations, showing the microscopic aspects of pus, micrococci, uric acid, cystin, blood discs, triple phosphates, &c.

Dr. Muter's work is, in short, a useful work of reference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 15, October 7, 1895.

An Ascent to the Summit of Mont Blanc, and on the Researches Executed during the Summer of 1895.—J. Janssen.—The author has studied the presence of watery vapour in the atmospheres of the sun. The spectrum was entirely deprived of its rays of an aqueous origin; all the group near D was absent, as well as that of C; *a* was so pale that it was difficult to decide if it was in its place. It was evident that on another step every aqueous manifestation would have disappeared.

Study of certain Meteorites.—Henri Moissan.—The author has resumed the study of certain metallic or holosideric meteorites in consequence of the discovery of a transparent diamond in the meteorite of Cañon Diablo. He arrives at the following conclusions:—In some holosideric meteorites there is no carbon; in others we find either amorphous carbon, or a mixture of this variety and of graphite. In a single meteorite, that of the Cañon Diablo, the author has found together the three varieties of carbon—diamond (black and transparent), graphite, and amorphous carbon.

Inflammability of "Fire-damp."—R. L. Devaux proposes to annul the inflammability of "fire-damp" by an admixture of carbon dioxide.

Mechanical Properties of the Alloys of Copper and Zinc.—Georges Charpy.—This paper can scarcely be regarded as a chemical communication. The most advantageous alloys are those containing from 30 to 43 per cent of zinc, and their value then diminishes rapidly. The elongation before rupture also increases with the proportion of zinc, and then decreases rapidly.

Glucinum Carbide.—P. Lebeau.—On heating in the electric furnace a mixture of glucinum oxide and of coke we have obtained, not the metal, but a definite carbide. Pure glucina was intimately mixed with half its weight of sugar charcoal. The mixture was agglommerated with a little oil and compressed into the form of small cylinders, which were then heated to incipient redness. The cylinders were then introduced into a tube of coke, closed at one end, and arranged in such a manner that the mixture was in the hottest part of the furnace. The current employed was of 950 ampères and 40 volts. The experiment required from eight to ten minutes. In a series of experiments with a current of 350 ampères and 50 to 60 volts, there was only obtained a nitride, or products containing nitrogen and carbon. Pure glucinum carbide appears in the form of yellowish brown microscopic crystals presenting hexagonal facets. It easily scratches quartz, and its specific gravity at 15° is 1·9. Chlorine attacks it readily at a dull red heat, forming a volatile chloride and a black residue of amorphous carbon and graphite. Bromine reacts at a rather higher temperature, and iodine has no action at 800°. Pure oxygen at dull redness produces a superficial oxidation. Vapour of sulphur reacts below 1000°, forming a sulphide. Phosphorus and carbon have no apparent action at dull redness. The composition of the carbide appears to be C_3Be_4. The atomic weight of glucinum should be close upon 14, and glucina should be a sesquioxide, Be_2O_3.

Researches on the Combinations of Mercury Cyanide with the Iodides.—Raoul Varet.—A thermochemical paper not of sufficient importance to warrant its insertion in full.

Double Decompositions ensuing between Mercury Cyanide and the Alkaline and Alkaline-earthy Metals.—Raoul Varet.—The fluorides, chlorides, sulphates, nitrates, carbonates, acetates, and picrates of these metals do not undergo double decomposition with mercury cyanide. With the bromides there is a slight double decomposition. With the iodides there is double decomposition, regulated by the production of the triple salts $HgCy_2$, MCy_2, HgI_2. With the sulphides there is complete double decomposition.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 12, 1895.

Certain Derivatives of the Bromides in C_3.—R. Lespieau.—An account of 1.2.3-tribromopropane; of 1.3-dibromopropane; of 1.3.3-tribromopropane oxymethane; 1.2-dibromopropene oxymethane; and 1-bromopropine oxymethane.

Benzinesulphoorthotoluidine and some of its Derivatives.—Ch. Rabout.—We see the great resistance of this sulphamide to oxidation, and its great stability in heat to the presence of dilute acids, notwithstanding its amidic character.

Determination of Organic Nitrogen by the Kjeldahl Process, in the absence of Nitrates.—H. Causse.

Volatile Acidity of Wines.—H. Jay.—The proportions of volatile acids found in French and Spanish wines of reliable origin oscillates between 0·38 and 0·80 grm. per litre, calculated as monohydrated sulphuric acid. On the contrary, all the Algerian wines which have been submitted to me contain per litre at least 1·30 grms., and in a majority of cases exceeding 1·60 grms.

Determination of Volatile Acids in Wines.—E. Burcker.

No. 13.

New Tube for Fractionated Distillations Modified by M. Lebel.—G. Berlement.—This apparatus cannot be described intelligibly without the accompanying figure.

New Researches on the Combination-heats of Mercury with other Elements.—Raoul Varet.—The heat disengaged in the combination of mercury with gaseous chlorine is +53·3 cal.; with liquid bromine, +40·6; with iodine, solid, +25·2 cal. (for the red compound) and 22·2 cal. (for the yellow compound); with oxygen, gaseous, +21·5 cal.

Isomeric Transformations of the Mercury Salts.—Raoul Varet.—A list of the heats developed by the mercurial compounds in their respective transformations.

Separation of Lime from Strontia and Baryta.—J. Dupasquier.

Action of Halogens on Methylic Alcohol.—A. Brochet.—This paper is not adapted for useful abstraction, and cannot claim insertion *in extenso*.

Preparation of the Amines of the Fatty Series.—A. Trillat.—The author gives an account of the preparation of monomethylamine, of the action of ammoniacal salts upon formaldehyd, the influence of reduction on the preparation of ethylamine.

Recognition of Alum in Wines.—M. Georges.—The author proposes the two following solutions:—1. Solution of pure tannin—Pure, 3·40 grms.; distilled water to make up 100 c.c. Each c.c. of this solution precipitates 0·005 grm. alumina, *i.e.*, the quantity contained in 0·0463 grm. of alum. 2. Solution of sodium acetate—($C_4H_3NaO_4,3H_2O_2$) or ($C_2H_3NaO_2,3H_2O$); neutral sodium acetate, crystalline, 24 grms.; distilled water to make up 100 c.c. Each c.c. of this solution contains a weight of combined acetic acid corresponding to 0·10 grm. monohydrated sulphuric acid. The author measures 20 c.c. of wine into a wide test-tube, and adds 2 c.c. of the solution of tannin. After agitation, he pours into the mixture 3 c.c. of the solution of sodium acetate, stirs again, and then leaves the mixture to settle, observing the phenomena produced. If, after five minutes, there appears a clotty precipitate we may assert the presence of alum. If the wine remains clear, or is at most slightly cloudy, the wine is genuine, or contains less than 1 decigrm. of alum per litre.

Existence of a Sulphuretted Substance in Cotton Oil.—J. Dupont.—American food-fats containing cotton oil have often become rancid, and in that state have a deceptive action with the silver nitrate. The author distils cotton-oil in a strong current of steam. The water collected has a disagreeable smell of a sulphuretted product. On successive treatments with ether there is obtained a small quantity of an oily matter which is attacked in the water-bath with nitric acid and potassium chlorate. If the excess of acid is driven off and the residue taken up in water the addition of barium chloride determines a strong precipitate of barium sulphate.

Use of Superphosphates.—Jules Joffre.—The author's experiments warrant the conclusion that the preferable action of superphosphate is not merely due to a more thorough dissemination in the soil, but to absorption of a part of the phosphoric acid in the state of compounds soluble in water. There is no proof that reverted phosphoric acid exists in the soil in the state of tricalcic phosphate.

Exposition of some Points concerning the Analysis of Fatty Substances.—G. Halphen.—The author gives, firstly, an examination of the physical characteristics, specific gravity, viscosity, spectroscopic behaviour, polarisation, solubility, congelation, expansion, and elastic conductivity. The physical methods just enumerated are not of themselves sufficient. Among the chemical methods, it is pointed out that Fauré's test, the action of chlorine gas, is not decisive; some vegetable oils are not bleached by this reagent, but turn brown; whilst some animal oils, especially that of the feet of horses, are blackened. The Welman's test and the phosphoric acid method are not trustworthy.

MISCELLANEOUS.

Hygienic Decision on Potable and Household Waters.—Prof. Flügge.—At the General Meeting of the German Association for the Care of Public Health, Prof. Flügge put forward the following propositions:—1. The customary hygienic decision on waters simply on the basis of a chemical, bacteriological, and microscopic examination of samples sent, is in almost every case to be rejected. 2. A single examination of water as to its admissibility for drinking or domestic consumption must, above all things, be followed by a visit of inspection to the place where the sample was taken. In many cases this examination alone leads to a conclusion that it may be supplemented by macroscopic inspection, and a determination of the hardness and the iron. In new installations the freedom of the water from micro-organisms should be ascertained. 3. The hygienic significance of remarkable analytical results can be generally ascertained only by repeated inspection and examination.—*Zeit. f. Angewandte Chemie.*

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1875.

NOTE ON THE REDUCTION OF THE OXIDES OF IRON BY MEANS OF CARBON MONOXIDE.

By ISAAC BRAITHWAITE.

FERRIC oxide, formed by igniting the precipitated hydrate, in granular powder which would pass through a sieve of 18 meshes to the inch, but not through one 28 to the inch, was heated in a porcelain tube to a low red heat. Successive small portions of CO were passed over it, each portion being passed back and forward repeatedly (from ten to twenty times) during a period of about five minutes (in some cases much longer). The proportion of CO_2 in each portion was determined by absorption in potash and weighing. This was repeated until the oxide was completely reduced to metallic iron. The results were not sufficiently accordant to warrant the giving of exact figures. Probably this may have arisen from several causes. The temperature may not have been sufficiently uniform, although one or two direct experiments showed no marked change in the results when the temperature was raised considerably above that usually adopted. The CO employed was not quite pure, and probably varied a little. The time during which each portion was allowed to act certainly affected the results; the most accordant ones being obtained when the action was prolonged many hours; but as some hundreds of successive portions were used, it was impracticable to allow so much time for each.

The facts ascertained may be stated generally thus:— At a low red heat, in presence of excess of Fe_2O_3, CO is completely (or almost completely) oxidised to CO_2. With excess of Fe_3O_4, rather more than two-thirds is oxidised to CO_2, the resulting mixture of gases being nearly $CO+2CO_2$. With excess of FeO, about one-third is oxidised, leaving the mixture nearly $2CO+CO_2$. When the iron is completely reduced, if the temperature falls below a dull red heat, there is considerable formation of CO_2 and deposit of carbon, probably from the formation and decomposition of iron carbonyl. The experiments were reversed by passing CO_2 over iron, and the action was proved to be reversible; that is, CO_2 passed over red-hot iron became two-thirds reduced; over FeO, one-third reduced; over Fe_3O_4, not reduced at all.

I am indebted to Mr. S. R. Rowling for the carrying out of these experiments.

A NEW FORM OF ACCUMULATOR.

By H. N. WARREN, Research Analyst.

THE invention relates to accumulators of a special type, whereby an extraordinary large surface of material is exposed. The negative element, consisting of a plate of pure porous lead, is manufactured for the purpose by partial compression in suitable moulds of spongy lead obtained by the slow precipitation of lead from a solution of the acetate by means of zinc; around this is compressed, again, an intimate mixture of metallic lead and litharge, made by melting lead in a deep clay crucible, and introducing into the same about 40 per cent of litharge, the whole being well stirred until cold. By this means a thorough incorporation of the litharge is obtained, the metallic appearance of the lead present being entirely masked. The metallic lead as produced in the first instance, together with the litherode lining, is tightly compressed into thin flat porous pots, each plate thus forming one negative element. For the construction of the positive plates is prepared an intimate mixture of lead peroxide, by first incorporating with the lead, as in the former instance, instead of litharge, barium carbonate; the resulting granular powder thus obtained being afterwards freed from the barium carbonate by digesting the same in hot hydrochloric acid, thus leaving the lead in a state of purity, which is afterwards mixed with a sufficiency of the plumbic peroxide and used as a charge for the positive cell, or to constitute, in other words, the positive plate. The resistance in such accumulators is very small, whereas at the same time they compare more favourably with others as regards their ampèrage. Plates of this description are now to be obtained at most of the leading electricians, and will be found highly beneficial to those requiring to demonstrate the practical construction, and at the same time the charging, of accumulators to classes or others; being rapidly charged by small batteries, and retaining the current admirably.

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

ON THE DETERMINATION OF ARGON.

By Th. SCHLŒSING, Jun.

SINCE argon has been discovered the question has been raised whether, like the other elements of the atmosphere, it interferes in the phenomena of life.

The experiments hitherto made on this point have given negative results. G. McDonald and A. M. Kellar have sought for argon in the composition of certain animals and certain seeds, but they have not met with it in an appreciable quantity. Nevertheless the subject is not exhausted, and it will doubtless be further examined, especially if argon plays a part in vegetable synthesis. For such a study it may be useful to determine with precision the argon contained in a given atmosphere. I have attempted this determination, to which I have been the more attracted because, independently of any physiological research, the determination of argon applied to normal air is doubtless of interest.

In consequence of its rarity we are naturally led to determine argon in very large volumes of air. But the measurement in the manifestation of large volumes of gases generally involves bringing them in contact with water, whence there result nearly always sensible errors. It is possible to obtain good results by operating only on volumes of air corresponding to 1·5 litres of nitrogen, and effecting all the measurements over mercury. We then employ for the separation of argon and nitrogen a system of apparatus of limited capacity, when it becomes easy to produce a vacuum, as well before the introduction of the gas to be measured as after its extraction, which constitutes a most precious resource.

After the example of Lord Rayleigh and Prof. Ramsay, to isolate the argon contained, *e.g.*, in normal air, I absorb the nitrogen of the air by means of magnesium after having eliminated the oxygen and the carbonic acid.

The arrangement for this purpose cannot be described intelligibly without the accompanying figure. The author's procedure has been carefully verified.

It has been enquired if argon treated in this manner is sufficiently purified. To ascertain this point I have taken specimens of the gas obtained in the determinations. Oxygen has been added, and the mixture has been submitted to the action of the spark in presence of potassa for eight hours. The oxygen has then been eliminated by means of pyrogallol and the gaseous residue measured anew. I have, *e.g.*, found:—Initial volume, 15·796 c.c.; final volume, 15·802 c.c. The difference is very small, and is of the degree of the errors of measurement.

I have made a global verification (so to speak) of the procedure. I prepared chemical nitrogen by passing over copper and copper oxide, at a red-heat, nitrous oxide obtained by the decomposition of ammonium nitrate. I measured this nitrogen after having added an accurately estimated volume of argon obtained from a determination conducted on my method. The proportions of the two gases was of the same degree as in the atmosphere. The mixture has undergone all the operations and manipulations indicated. I compared the volume of argon introduced to that of the argon recovered. Three experiments of this kind gave:—

	Gaseous mixture introduced.				
	Argon.	Chemical Nitrogen.	Argon recovered.	Loss. Total.	Percentage of the Argon introduced.
1.	18·138 c.c.	1395·6 c.c.	18·008 c.c.	0·130	0·72 c.c.
2.	18·155 ,,	1409·2 ,,	18·083 ,,	0·072	0·40 ,,
3.	16·936 ,,	1288·1 ,,	16·809 ,,	0·127	0·75 ,,

These figures give an idea of approximation obtained. I shall return to the cause of the small loss observed, and give an account of the determinations effected both of normal air and of other gaseous mixtures, such as those extracted from the soil. At present I will merely say that normal air yielded as a mean (number obtained without correction) 1·183 vol. of argon to 100 vols. of atmospheric nitrogen (nitrogen and argon), or 0·935 vol. to 100 vols. air, figures which approximate in deficiency to less than 100 of their value.—*Comptes Rendus*, cxxi., p. 525.

DETERMINATION OF HEAVY METALS BY TITRATION WITH SODIUM SULPHIDE.

By G. NEUMANN.

It is known that most alkaline metals are precipitated quantitatively from their solutions by an alkaline sulphide. This reaction is utilised by mixing the metallic solution in question with a known excess of the precipitant, and titrating back the excess of sulphide. As the alkaline sulphides have an alkaline reaction, we might expect that the object might be attained without using an excess of alkaline sulphide by taking litmus or phenolphthalein as an indicator as in the titration of acids. Experiments in this direction, however, proved useless, since alkaline sulphides, like hydrogen sulphide, destroy the colour of the indicator.

On this account the neutral metallic salt to be analysed was placed in a measuring flask along with a considerable excess of a dilute standardised solution of an alkaline sulphide, and the flask was filled up to the mark with water. As the precipitates formed are sometimes not very dense and do not readily subside, there was added in most cases a 20 per cent solution of sodium chloride *before* filling up to the mark, and the liquid well shaken and thus quickly clarified. An aliquot part of the clear liquid was boiled with a measured excess of decinormal sulphuric acid until the vapour on being tested with moist lead paper was found free from hydrogen sulphide, and was then titrated back with decinormal potassa, using phenolphthalein as an indicator. The quantity of metal originally present may then be calculated. An example may explain these general indications. For standardising the sodium sulphide there were taken decinormal potassa, (?) decinormal sulphuric acid. 17·1 c.c. of the solution of sodium sulphide was boiled with 30 c.c. sulphuric acid until all sulphuretted hydrogen was expelled, and used with phenolphthalein as indicator, 11·8 c.c. potassa for neutralisation, whence the sodium sulphide was calculated as 1·05/10 normal.

With this solution we titrated, *e.g.*, 1/5 normal solution of potassium chrome alum. 25 c.c. of this liquid were mixed in a 200 c.c. flask with 20 c.c. of a 20 per cent solution of sodium chloride and 50 c.c. of the above solution of sodium sulphide, and filled up to the mark. After shaking up the contents of the flask, green chromium hydroxide quickly subsided. 50 c.c. of the liquid were poured through a folded filter and boiled with 5 c.c. of sulphuric acid until the complete expulsion of the sulphuretted hydrogen, and titrated back with 4·8 c.c. potassa.

From these data there was calculated a proportion of 0·526 per cent Cr_2O_3 as against 0·51 per cent theoretically.

The author has shown that the method is widely applicable, as he has made experiments with ordinary alum, potassium-chrome alum, ferro-ammonium sulphate, ferric chloride, manganese-ammonium sulphate, nickel ammonium sulphate, cobalt, zinc, and copper sulphates, lead and silver nitrates, and cadmium sulphate.

With metals, the sulphides of which are readily separated in a granulated state, the addition of sodium chloride was sometimes omitted. In some metals, the salts of which are precipitable by sulphuretted hydrogen in an acid solution, and those, such, *e.g.*, as copper, form colloidal sulphides on the addition of sodium sulphide, the separation of the sulphide was effected by the addition of an acid. The analysis was then effected by heating the mixture of metallic salt and sodium sulphide in a measuring flask with a measured excess of sulphuric acid until the reaction of sulphuretted hydrogen no longer appeared, filling up to the mark when cold and titrating a filtered aliquot part with potassa. The author has applied this method in determinations of lead as well as of copper.

The method is of course only applicable if the salts under examination are neutral. If acid the free acidity must be expelled prior to titration. Most chlorides lose their excessive hydrochloric acid if they are dried up on the water-bath, taken up in alcohol and again dried. Such experiments were effected with an acid solution of zinc and copper. Here a three-fold evaporation with alcohol at 97 per cent was the most favourable. After a fourth evaporation from alcohol, the residue did not yield a clear solution. The evaporation is effected very rapidly if air is blown upon the surface of the liquid. Sulphates are previously converted into acid chlorides by treatment with barium chloride and hydrochloric acid. This is best effected in a measuring flask, and an aliquot part is then drawn off with a pipette as above described.

Nitrates must be twice evaporated down with concentrated hydrochloric acid, and then made neutral as already described. — *Zeitschrift fur Analyt. Chemie*, xxxiv., p. 454.

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Continued from p. 196).

Experimental Results with Mixtures of Normal Liquids.

In the following Tables (II. to IX.) are given those data of the experiments necessary for the calculation of the vapour-tensions. The superscriptions over each column of data render any preliminary mention here unnecessary.

Relations between the Vapour-tensions, Partial and Total, and the Concentration of the Liquid Phases.

We remark first, that the tension of the mixed vapour emitted by any of the mixtures of volatile liquids examined is always greater than the tension of the less volatile liquid and always less than that of the more volatile liquid; also, that the partial tension or pressure

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* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

Table II.—*Vapour-Tensions of Mixtures of Benzene and Monochlorbenzene at 34·8°.*

Vapour-tension of Benzene at 34·8° is 145·4 m.m. of Mercury.
Vapour-tension of Chlorbenzene at 34·8 is 20·3 m.m. of Mercury.

Mols. C_6H_5Cl in 100 mols. of liquid mixture.	Mols. C_6H_5Cl in 100 mols. of gaseous mixture.	Grms. C_6H_5Cl in vapour.	Grms. C_6H_6 in vapour.	Tension of C_6H_5Cl in m.m.	Tension of C_6H_8 in m.m.	Volume of air in m.m.	Barometer in m.m.	Internal pressure in m.m.
15·18	1·33	0·0454	2·3075	1·7	124·6	3782	763	11
29·08	6·11	0·0857	0·9143	6·6	101·3	1900	757	17
65·06	19·37	0·1800	0·5202	12·3	51·3	2032	758	18
79·21	35·15	0·3572	0·4750	19·1	27·9	3787	756	12

Table III.—*Vapour-Tensions of Mixtures of Toluene and Monochlorbenzene at 34·8°.*

Vapour-tension of Toluene at 34·8° is 46·8 m.m. of Mercury.
Vapour-tension of Chlorbenzene at 34·8° is 20·3 m.m. of Mercury.

Mols. C_6H_5Cl in 100 mols. of liquid mixture.	Mols. C_6H_5Cl in 100 mols. of gaseous mixture.	Grms. C_6H_5Cl in vapour.	Grms. C_7H_8 in vapour.	Tension of C_6H_5Cl in m.m.	Tension of C_7H_8 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
18·96	9·84	0·0510	0·3821	4·3	38·2	1963	757	17
41·82	22·66	0·0985	0·2754	8·1	27·6	1973	760	21
76·71	67·79	0·2089	0·0821	17·5	8·2	1965	757	18

Table IV.—*Vapour-Tensions of Mixtures of Benzene and Monobrombenzene at 34·8°.*

Vapour-tension of Benzene at 34·8° is 145·4 m.m. of Mercury.
Vapour-tension of Brombenzene at 34·8° is 8·0 m.m. of Mercury.

Mols. C_6H_5Br in 100 mols. of liquid mixture.	Mols. C_6H_5Br in 100 mols. of gaseous mixture.	Grms. C_6H_5Br in vapour.	Grms. C_6H_6 in vapour.	Tension of C_6H_5Br in m.m.	Tension of C_6H_6 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
30·33	24·30	0·0395	0·4975	2·6	103·1	1018	757	13

Table V.—*Vapour-Tensions of Mixtures of Benzene and Chloroform at 34·8°.*

Vapour-tension of Benzene at 34·8° is 145·4 m.m. of Mercury.
Vapour-tension of Chloroform at 34·8° is 289·2 m.m. of Mercury.

Mols. $CHCl_3$ in 100 mols. of liquid mixture.	Mols. $CHCl_3$ in 100 mols. of gaseous mixture.	Grms. $CHCl_3$ in vapour.	Grms. C_6H_6 in vapour.	Tension of $CHCl_3$ in m.m.	Tension of C_6H_6 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
16·97	24·30	0·3243	0·6607	39·6	123·5	1032	755	25
50·53	63·74	1·1513	0·4187	130·7	74·3	1030	756	25
59·47	73·25	1·4770	0·3531	162·2	59·2	1030	749	25

Table VI.—*Vapour-Tensions of Mixtures of Toluene and Chloroform at 34·8°.*

Vapour-tension of Toluene at 34·8° is 46·8 m.m. of Mercury.
Vapour-tension of Chloroform at 34·8° is 289·2 m.m. of Mercury.

Mols. $CHCl_3$ in 100 mols. of liquid mixture.	Mols. $CHCl_3$ in 100 mols. of gaseous mixture.	Grms. $CHCl_3$ in vapour.	Grms. C_7H_8 in vapour.	Tension of $CHCl_3$ in m.m.	Tension of C_7H_8 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
28·74	65·29	0·4856	0·1994	64·7	34·4	1040	747	24
60·43	89·20	1·3578	0·1270	160·9	19·5	1031	754	23

Table VII.—*Vapour-Tensions of Mixtures of Benzene and Carbon Tetrachloride at 34·8°.*

Vapour-tension of Benzene at 34·8° is 145·4 m m. of Mercury.
Vapour-tension of Carbon Tetrachloride at 34·8° is 169·4 m.m. of Mercury.

Mols. CCl_4 in 100 mols. of liquid mixture.	Mols. CCl_4 in 100 mols. of gaseous mixture.	Grms. CCl_4 in vapour.	Grms. C_6H_6 in vapour.	Tension of CCl_4 in m.m.	Tension of C_6H_6 in m.m.	Volume of air in c c.	Barometer in m.m.	Internal pressure in m.m.
7·21	9·66	0·1741	0·8260	14·5	135·4	1205	762	18
18·68	20·54	0·3931	0·7561	32·5	125·5	1205	758	20
28·00	35·71	0·6267	0·5730	60·0	105·0	1016	756	12
50·19	55·03	1·1231	0·4666	91·3	75·6	1201	762	19
63·88	65·27	1·2699	0·3431	103·1	54·5	1219	760	27
77·89	83·01	1·5321	0·1669	117·6	31·8	1034	754	26

Table VIII.—*Vapour-tensions of Mixtures of Toluene and Carbon Tetrachloride at 34·8°.*

Vapour-tension of Toluene at 34·8° is 46·8 m.m. of Mercury.
Vapour-tension of Carbon Tetrachloride at 34·8° is 169·4 m.m. of Mercury.

Mols CCl_4 in 100 mols. of liquid mixture.	Mols. CCl_4 in 100 mols. of gaseous mixture.	Grms. CCl_4 in vapour.	Grms. C_7H_8 in vapour.	Tension of CCl_4 in m.m.	Tension of C_7H_8 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
30·69	58·19	0·4754	1·2046	51·5	37·0	1016	756	12
53·85	67·86	0·9305	0·1260	78·3	22·3	1022	758	17
60·00	83·67	0·9624	0·1126	99·1	19·4	1020	759	14
91·87	97·22	1·6063	0·0281	155·1	4·5	1017	756	13

TABLE IX.—*Vapour-Tensions of Mixtures of Nitrobenzene and Carbon Tetrachloride at 34·8°.*

Vapour-tension of Nitrobenzene at 34·8° is 1·16 m.m. of Mercury.
Vapour-tension of Carbon Tetrachloride at 34·8° is 169·4 m.m. of Mercury.

Mols. CCl_4 in 100 mols. of liquid mixture.	Mols. CCl_4 in 100 mols. of gaseous mixture.	Grms. CCl_4 in vapour.	Grms. $C_6H_5NO_2$ in vapour.	Tension of CCl_4 in m.m.	Tension of $C_6H_5NO_2$ in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
5·37	93·51	0·3095	0·0175	18·9	1·3	19·73	760	20
50·73	94·47	1·1111	0·0489	113·9	6·2	1020	756	12
73·54	96·09	1·4420	0·0471	141·5	5·6	1022	753	18
95·21	98·61	1·7798	0·0190	167·6	2·3	1022	753	18

of either component, of any mixture, is always less than the vapour-tension of the component in a state of purity;* these two properties belong to all the mixtures investigated. In the discussion of the other properties, we shall find it convenient to divide the mixtures into classes. In the first class we put the mixtures of benzene and toluene with monochlor- and monobrombenzene; in the second, the mixtures of chloroform with benzene, and with toluene; in the third, the mixtures of carbon tetrachloride with toluene, and with benzene; and in the fourth and last, the mixture of nitrobenzene and carbon tetrachloride.

Now the mixtures of the first class are made up of liquids which are very simular in their chemical constitution, and it is natural to expect that they will exhibit the very simplest phenomena when mixed with one another. And, indeed, this expectation is realised, for the vapour-tensions of their mixtures are seen to be linear functions of the concentration: in the graphic representations (abscissæ = molecular percentages; ordinates = vapour-tensions) of the determinations, these fall upon or very close to the straight lines connecting the points on the axes of ordinates corresponding to the vapour-tensions of each of the pure liquids. In order to find the vapour-tension of any mixture of these liquids, all that is necessary to do is to connect on the axis of ordinates, the points representing the vapour-tensions of the two liquids in a state of purity, by a straight line, and where the perpendicular to the axis of abscissæ cuts this line, the value of the ordinate corresponding to the point of intersection gives the vapour-tension of the chosen concentration; of course, partial tensions can be found in a similar way. Also, by the application of the "rule of mixtures," it is easy to calculate the total or partial tensions. It may be worth while to remark, in passing, that these four liquids, which we have put in a class by themselves, are just those which verify by far the best the generalisations of van der Waals; undoubtedly, these liquids are to be reckoned as in the highest degree "normal," as their behaviour approaches most nearly that theoretically predicted.

In the second of our classes we find a different behaviour. When chloroform is added to benzene or to toluene, the total vapour-tension is less than that resulting from the calculation by the rule of mixtures; the variation reaches a maximum when 100 molecules of the mixture contain from 50 to 60 molecules of chloroform; the curve then tends to approach the straight line connecting the points on the axis of ordinates representing the vapour-tensions of the pure liquids, practically coinciding with it when the number of chloroform molecules has passed 80. The depression of the vapour-tension of chloroform, caused by the addition of either benzene or toluene, is linearly proportional to the concentration only in solutions containing less than 20 molecules of either hydrocarbon to 100 molecules of the mixture.

When we consider the partial tensions of these mixtures, we see that the same regularity as was observed in the first class of liquids is found here, but only for toluene and benzene; the partial tension curve for chloroform resembles closely in its contour that for the total tension of the mixture. The departure of chloroform from the straight line is not, however, very marked.

In the third class of mixtures we meet with a different behaviour. When benzene or toluene is added to carbon tetrachloride, we observe that the curve of total tension follows closely the line connecting the points corresponding to the vapour-tensions of the mixed liquids until towards the abscissæ value of 80; the curve then commences to fall, only to rise again, and pass above the straight line, when, finally, it changes its direction to fall upon the axis of ordinates at the point standing for the vapour-tension of the pure hydrocarbon, benzene, or toluene, as the case may be. As is seen, the curve has three turning points. The curve of the partial tension of the carbon tetrachloride resembles in every detail, in each mixture, that of the total tension; but once more it is observed that the partial pressure curve for the hydrocarbons is, so to say, a straight line. It is truly a remarkable result that in the mixtures which have such different total tension curves, the curve for these two liquids should turn out so simple. There is but little doubt that the above instances are sufficient to render very probable the assumption that this behaviour is general, and that in all biniary mixtures made up of benzene or toluene, with any other volatile liquid whatsoever, the same normality in the behaviour as regards partial vapour-tension of these two hydrocarbons will be found. It is even possible to go a step farther, and claim that, inasmuch as in the mixtures of the first class, normality of the partial pressure was found in the case of each component of the mixture, this normality will persist in mixtures of the halogen compounds of benzene with any other liquids.

The fact that benzene and toluene possess "straight line" partial pressure curves will enable us to get reliable and important information as to the partial pressures of other liquids mixed with either of the hydrocarbons, from a knowledge of the total pressure of the mixtures; for all that is necessary to do is to draw, in the coordinate system adopted in this paper, the total pressure curve and a straight line from the point, representing, on the axis of ordinates, the vapour-tension of benzene at the temperature at which the determination has been made, to the foot of the opposite ordinate; the value of any ordinate comprised between these two curves gives, then, the partial pressure, to a very close approximation, of the other component of the mixture.

Furthermore, it is apparent that the partial tensions of either chloroform or carbon tetrachloride is the same when mixed in the same proportions with either benzene or toluene; the simplicity of the behaviour of the latter liquids permits of the free exhibition of the peculiarities in that of the former.

(To be continued).

Experiments on the Reductive Power of Pure Yeasts: Means for its Measurement.—M. Nastukoff. Taking the power of the ferment of champagne as 1·00, that of the wines of Portugal is 0·75, of *Saccharomyces pastorianus* 0·50, that of *S. apiculatus* 0·25, and that of the yeast of Brussels beer 0·25.—*C. R.*, cxxi., No. 16.

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* This observation does not seem to be confirmed in the case of the partial pressure of nitrobenzene in its mixture with carbon tetrachloride. This exception, however, I am inclined to attribute to experimental errors, which made themselves particularly felt in the investigation of mixtures of these two liquids. Indeed, if the allowance be made for the degree of accuracy which we have decided the method capable of yielding, it will be seen that the discrepancy can be made to disappear almost entirely.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 205).

On the Gases used.—In all my fundamental experiments I used none but air, oxygen, hydrogen, and coal-gas, stored for *at least twenty-four hours* in large gasometers over water free from organic matter, and made alkaline with lime or baryta to absorb carbonic anhydride. The gasometer used to hold oxygen was one of Pepys's; it held about 1 cubic metre; it was made of copper, and would stand a pressure of 5 atmospheres. The gasometers used for storing air, hydrogen, or coal-gas were bell-shaped and properly counterpoised; they were built of galvanised sheet-iron; they held about 5 cubic metres, and were placed in the basement of the large laboratory, where the tank of alkaline water was put in winter to keep it from freezing.

All tubes connecting the gasometers to the burner were made of lead; they were long and very flexible, so as to yield easily to all requirements; they were washed successively with ammoniated water, pure water, water acidulated with sulphuric acid, and, lastly, with pure water, taking care to leave their inner surface damp.

It was only by the above means that I succeeded in obtaining air, oxygen, and hydrogen completely free from sodium. I always found illuminating gas free from sodium when taken direct from the main.

On the Air.—I have already explained the methods I adopted for obtaining air free from sodium; I need not repeat them.

On the Oxygen.—The oxygen was prepared by the action of heat on a mixture of chlorate of potassium and *red oxide of manganese*, calcined and washed. Before letting it into the gasometer filled with alkaline water, it was made to pass through three tubulated bottles, the first containing a concentrated solution of hydrate of potassium, and the other two pumice-stone broken up and soaked in a saturated solution of the same hydroxide. After twenty-four hours rest, it was free from all trace of sodium or potassium compounds.

On the Hydrogen.—I have had great difficulty in getting pure hydrogen,—that is to say, hydrogen burning in pure air with a *colourless* flame, and showing neither the sodium line nor any trace of a continuous spectrum.

I will begin by confessing that I utterly failed to obtain hydrogen which would burn with a colourless flame so long as I used it as fast as I made it. Therefore hydrogen made by the electrical decompostion of water, acidulated with sulphuric acid, in the presence of pure zinc amalgam to retain the oxygen, did not fulfil this condition. It was absolutely necessary to pass it through pure *boiling* water, to condense the steam in a metallic refrigerator, and to collect and store it for at least twenty-four hours over pure water. I will say the same for hydrogen prepared from zinc and a 10 per cent solution of sulphuric acid. However pure the metal, acid, and water might be, the resultant hydrogen, when ignited at the end of a platinum tube, free from dust, which had been raised to white-heat and then suddenly cooled, burnt in pure air with a reddish-yellow flame, unless it had been passed through pure boiling water and then stored over pure water. The hydrogen used in all my principal experiments was obtained from zinc specially prepared for these researches. More than 40 kilogrammes of this zinc was used. It was freed from all traces of carbon, arsenic, and other bodies likely to form compounds when in a gaseous state. It was made from pure calamine, and had been re-distilled in bulk with well-calcined oxide of zinc, to remove all traces of carbon, and condensed in a fire-clay retort.*

I facilitated the production of hydrogen by making the zinc reaction take place in pure boiling water, to which was added, little by little, sulphuric acid mixed with an equal volume of water *saturated with sulphate of copper*, so as to yield a steady current of gas.

By placing the receiving vessel, sometimes glass but generally lead, in a bath of water kept running to prevent rise in temperature, one can obtain hydrogen free from sulphurous or sulphuric acid. In addition to this, during my first trials, I took care, before passing the hydrogen into the gasometer, to pass it through a large flask filled with pumice-stone, broken into very small pieces and moistened with a solution of caustic potash, and a second large flask filled with small pieces of pumice-stone moistened with an acid solution of sulphate of silver. Whenever the rate of evolution of hydrogen did not exceed 100 litres an hour—and care was taken to keep the glass or lead generator at a low temperature—I was unable to detect the formation of either sulphate or sulphide of potassium or sulphide of silver.

This hydrogen, when received into the gasometer, and tested directly after its preparation, even after passing through pure boiling water, burns with a slightly luminous flame, sometimes slightly yellow, sometimes slightly orange or even reddish; but it is noticeable that, in proportion as it is left over water made alkaline by lime or baryta, so it loses this property until it is entirely deprived of it. Notwithstanding the numerous trials to which I have subjected it, I have not succeeded in determining the nature of the substance which gives hydrogen the property of burning with a *slightly reddish* flame.* So long as the flame has the least yellowish tint, spectrum analysis shows the sodium D line in it. In order to guard against atmospheric impurities I took the precaution, during my experiments, of effecting the combustion of hydrogen in an inverted bell-jar holding 20 litres, with a neck the edge of which was ground and polished, closed by a flat metal lid, which was also ground and polished, kept at a low temperature by cold running water. The bell-jar, whose surface was damp, was filled with air continually renewed from the *top*, and freed from sodium by the method mentioned above. A metal tap was screwed into a hole in the centre of the cover, so as to enable me to renew the air conveniently, and the tap was put into direct communication with the domed gasometer filled with purified air. I was thus able to satisfy myself that the colouring of the hydrogen flame was as often due to the surrounding air as to the hydrogen itself, and that this latter case occurs *always when one tries to burn the gas as soon as it is made.*

In pure air and complete darkness, pure hydrogen—issuing from a clean platinum burner—burns with a flame so devoid of brilliancy, *so little luminous*, that I was often obliged to put a piece of platinum wire in it in order to see it. The invisibility of the hydrogen flame is furthermore shown by the introduction of oxygen, and even of pure air. Thus when the height of the flame is diminished one-half by the presence of oxygen, the hydrogen becomes *incandescent*—that is to say, *luminous*—when burning, and one notices *a deep and very pure blue light*, always supposing that the air and oxygen supplied are free from sodium. If the hydrogen or the air show traces of so-

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* The hydrogen used in the hydrogen and air blowpipe was made from pure calamine zinc kept melted for some time, and well stirred up with 5 per cent of its weight of powdered fused litharge. The alloy of zinc and lead made thus is free from all trace of carbon; with a 10 per cent solution of sulphuric acid it gives off with great ease hydrogen, which, after remaining twenty-four hours in a gasometer in contact with alkaline water free from organic matters, burns in pure air with a colourless flame. Having ascertained that hydrogen set free by the action of zinc and lead on dilute sulphuric acid was, by remaining over alkaline water, entirely deprived of the property of burning with a slightly luminous flame, I henceforth used only hydrogen prepared in this manner in the hydrogen and air blowpipe. But in this case I have always interposed a glass bottle, 12 litres capacity, with two stopcocks filled with small pieces of pumice-stone moistened with a strong solution of caustic potash, and a counterpoised zinc-domed gasometer, 1 cubic metre capacity, charged with baryta water, between the leaden flask with stopcocks, in which the gas was produced, and the burner used to burn it.

* For researches made on this subject, see Note (Chem. News, vol. lxxii., p. 190).

dium, the light is a pale and slightly greenish blue. I have already mentioned that as soon as hydrogen is brought to incandescence, platinum melts in it, and spectrum analysis of the flame shows a *continuous* spectrum. On increasing the volume of oxygen, so as to reduce the flame to about four-fifths of its height, the blue colour is not increased—on the contrary, it appears diminished; at the same time the continuous spectrum gains in clearness; one sees indications of the appearance of lines; but in spite of all efforts it was impossible for me to determine their position in a spectrum which, I repeat, was *too strongly luminous*.

I did not succeed in getting hydrogen to burn in an excess of oxygen by the method I employed; every time I supplied oxygen sensibly in excess of half the volume of hydrogen, combustion started in the platinum nozzle and from thence extended to the pipe of the burner itself, which, although of platinum, began to melt. I consider the combustion of hydrogen in a sensible excess of oxygen to be impracticable with the blowpipe used by Mr. G. Matthey, even under a pressure of two atmospheres.

(To be continued).

THE DETERMINATION OF SELENIOUS ACID BY POTASSIUM PERMANGANATE.*

By F. A. GOOCH and C. F. CLEMENS.

The fact that sulphurous and tellurous acids may be oxidised quantitatively by a sufficient excess of potassium permanganate suggests naturally the application of the same general method to the determination of selenious acid. It is the object of this paper to record the results of experiments in this direction.

Brauner (*Journ. Chem. Soc.*, 1891, p. 238) found that in the action of the permanganate upon tellurous acid, whether in a solution acidified with sulphuric acid or made alkaline by caustic soda, the reduction of the permanganate does not proceed to the lowest degree of oxidation, the tellurous acid being unable to reduce the higher hydroxides of manganese which separate. In employing the reaction quantitatively it is necessary, therefore, to add the permanganate in distinct excess, and then to destroy the surplus by means of standard oxalic acid added to the solution acidified with sulphuric acid, subsequently determining the excess of oxalic acid in the warmed solution by addition of more permanganate. The difference between the amount of permanganate actually used and that required to oxidise the known amount of oxalic acid introduced should naturally be the measure of the tellurous acid acted upon. Brauner found, however, an error in the process, by no means inconsiderable, due to the decomposition of the permanganate outside the main reaction. In a subsequent paper from this laboratory (Gooch and Danner, *Amer. Journ. of Science*, xliv., 301) it was shown that if the precaution is taken to restrict the amount of sulphuric acid present in the solution when the permanganate acts, the secondary decomposition involving loss of unutilised oxygen is kept within narrow bounds. In our work upon the oxidation of selenious acid we have followed the suggestions gained in the treatment of tellurous acid by Brauner's method.

The selenium dioxide which we employed was prepared from so-called pure selenium by dissolving the element in strong nitric acid, removing the nitric acid by evaporation, treating the aqueous solution with barium hydroxide to throw out any selenic acid formed in the oxidation, evaporating the solution to dryness, and subliming and resubliming the residue in a current of dry air until the product was white. The oxide thus prepared was weighed out for individual experiments or was dissolved in a standard solution from which definite portions were drawn for use.

In the first series of experiments, the results of which are recorded in Table I., the selenium dioxide was dissolved in 100 $c.m.^3$ of water, 10 $c.m.^3$ of sulphuric acid of half strength were added; an approximately decinormal standardised solution of potassium permanganate was added until the characteristic colour predominated over that of the brown hydroxide deposited during the oxidation; oxalic acid in solution of known strength was introduced until the excess of permanganate had been destroyed and the insoluble hydroxide dissolved; and, finally, after heating the solution to about 80° C., more of the permanganate was added to the colour reaction. The final volume varied from 250 $c.m.^3$ to 350 $c.m.^3$, so that the sulphuric acid (absolute) present varied from about 5 per cent at the start to from 1½ to 2 per cent at the end.

When the permanganate is first introduced into the acidified solution the colour vanishes, leaving a clear colourless liquid; but as more is added the solution becomes yellow, and deepens gradually in colour to a reddish-brown, until turbidity, due to the deposition of a brown hydroxide of manganese, ensues, and finally the characteristic colour of the permanganate is plainly distinguishable. The exact point at which precipitation of the manganic hydroxide begins depends upon the dilution, acidity, and temperature of the solution. In experiments (1) and (2) the permanganate was added to the cold solution at the first, but the liquid was heated after the addition of oxalic acid, and before the final titration with the permanganate. The remaining determinations of the series were made in solutions kept hot throughout.

TABLE I.

[Se = 79·1, O = 16.]

	SeO_2 taken.	Oxygen equivalent of permanganate used.	Oxygen equivalent to oxalic acid used.	SeO_2 found.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.
(1)	0·1000	0·03026	0·01571	0·1010	0·0010+
(2)	0·1002	0·03038	0·01578	0·1014	0·0012+
(3)	0·0997	0·02634	0·01182	0·1008	0·0011+
(4)	0·0999	0·02568	0·01122	0·1004	0·0005+
(5)	0·1000	0·02536	0·01077	0·1012	0·0012+
(6)	0·1000	0·03226	0·01765	0·1015	0·0015+
(7)	0·1001	0·04455	0·02992	0·1016	0·0015+
(8)	0·2001	0·05448	0·02543	0·2018	0·0017+
(9)	0·1997	0·05219	0·02318	0·2014	0·0017+
(10)	0·1997	0·05215	0·02318	0·2011	0·0014+
(11)	0·5178	0·13215	0·05721	0·5203	0·0025+
(12)	0·5197	0·14105	0·06541	0·5252	0·0355+

An examination of these results develops the fact that the action proceeds regularly in the main under the conditions of experimentation, but that there is an apparent waste of permanganate in the process. It was observed that the addition of a little permanganate beyond the exact amount necessary to produce the end-reaction occasioned the precipitation of manganese hydroxide, evidently, according to Guyard's reaction, by interaction between the permanganate and the manganous sulphate present. Plainly the amount of sulphuric acid present, which we kept purposely low to obviate the spontaneous decomposition of the permanganate, was not sufficient to prevent the ultimate formation of the hydroxide at the temperature of action. The natural inference is that the difficulty in the determinations may have been due rather to an interference with the colour reaction at the end of the oxidation process, due to the incipient tendency of the permanganate to act upon the manganous salt, than to direct loss of oxygen from the permanganate. If this is true, the obvious and simple remedy should be found in effecting the oxidation of the oxalic acid at the end of the process at a temperature so low that the inclination

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* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. l., July, 1895.

of the permanganate and manganous sulphate to interact shall be diminished. Table II. contains the record of experiments in which this precaution was taken. The entire process of oxidation, which was otherwise similar to that of the previous experiments, was brought about between the temperature of 75° C. at the beginning and 50° C., or even a little less, at the end. The end-reaction was in every case sharp, and the final colour was permanent for several minutes at the least.

Table II.

	SeO_2 taken. Grm.	Oxygen equivalent of permanganate used. Grm.	Oxygen equivalent to oxalic acid used. Grm.	SeO_2 found. Grm.	Error. Grm.
(13)	0·1000	0·03506	0·02065	0·1001	0·0001 +
(14)	0·1000	0·03519	0·02073	0·1004	0·0004 +
(15)	0·1000	0·03706	0·02255	0·1007	0·0007 +
(16)	0·1000	0·03853	0·02422	0·0994	0·0006 −
(17)	0·1000	0·03512	0·02065	0·1005	0·0005 +
(18)	0·2000	0·06124	0·03256	0·1994	0·0006 −
(19)	0·2011	0·06069	0·03177	0·2008	0·0003 −
(20)	0·2004	0·06072	0·03177	0·2010	0·0006 +
(21)	0·2020	0·06083	0·03185	0·2012	0·0008 −
(22)	0·2038	0·06106	0·03185	0·2028	0·0010 −

These results are evidently an improvement upon those of the first series of experiments, and are fairly satisfactory so far as concerns the estimation of the amounts of selenium dioxide discussed. The determination of large amounts of selenious acid by this method is somewhat less advantageous than it would be if the reduction of the permanganate proceeded farther in the first action. One hundred c.c. of a standard solution is as much as can be conveniently handled in a single process of titration, and that volume of decinormal permanganate (which is about as strong as the standard solution should be when accurate work is expected) is capable of oxidising about 0·25 grm. of selenium dioxide.

The process which we recommend consists, in brief, in the addition of standard potassium permanganate to the solution of selenious acid containing not more than 5 per cent of its volume of strong sulphuric acid, the introduction of standard oxalic acid until the liquid clears, and the titration of the excess of oxalic acid by permanganate, at a temperature not much exceeding 50° or 60° C. The permanganate and the oxalic acid should be standardised under similar conditions of acidity and temperature, and for a standard of final reference we prefer pure crystallised ammonium oxalate.

We have made experiments in which the initial oxidation of the selenious acid was made in alkaline solution, but inasmuch as the amount of permanganate required for the oxidation is about three times as great as that needed in the acid solution, the treatment in alkaline solution is practically inferior.

THE ESTIMATION OF THE HALOGENS IN MIXED SILVER SALTS.

By F. A. GOOCH and CHARLOTTE FAIRBANKS.

Known methods for the estimation of chlorine, bromine, and iodine in mixed silver salts depend either upon the reduction of the salts to metallic silver or their conversion to a single definite silver salt. The old but by no means ideal methods for the determination of chlorine and bromine in mixed silver chloride and bromide, by reduction of the salts to silver in hydrogen at high temperatures or conversion to silver chloride in an atmosphere of chlorine, are typical. Perhaps the best of all are the electrolytic method of Kinnicutt (*Am. Chem. Jour.*, iv., 22) for the reduction of the fused chloride and bromide, the battery process of Whitfield (*Am. Chem. Journ.*, viii., 421), which involves the electrolysis of the solution of the silver salts in potassium cyanide, and the method of Maxwell-Lyte (Chem. News, xlix., 3), according to which the silver in the cyanide solution of the silver salts is thrown down by potassium iodide and sulphuric acid. Even in these processes there are points against which objection may be raised with reason. Thus, in the processes of Whitfield and Maxwell-Lyte, it is next to impossible to secure complete and speedy solution of the dried silver salts in potassium cyanide without recourse to intermediate washing and treatment with nitric acid; and in Kinnicutt's method, which has been applied only to the analysis of the mixed chloride and bromide, difficulty is found in the speedy removal of all sulphuric acid from the spongy mass of silver formed in the reduction.

We have tried many experiments with a view to simplifying the analysis of the mixed silver salts. Ignition with mercuric cyanide according to Schmidt's method for sulphides (*Ber. d. Chem. Gesell.*, xxvii., 225); treatment with cuprous chloride dissolved either in ammonia or in hydrochloric acid; the action of ferrous oxalate dissolved in potassium oxalate, Eder's reagent (*Ber. d. Chem. Ges.*, xiii., 500); treatment with chromous chloride or chromous acetate; contact with powdered magnesium under dilute acid; and many other plans of action with powerful reducers have failed to yield analytical results comparable with those of the known methods. Hydrogen sulphide, dry or moist, and ammonium sulphide attack the halogen salts of silver with varying intensity, the chloride very easily, the bromide with less ease, and the iodide most difficultly—as might be predicted from a knowledge of the thermal values involved in the reactions. A current of hydrogen sulphide charged with ammonium sulphide effects the complete conversion of silver chloride to silver sulphide at a temperature below 200° C,; but we have never succeeded in securing absolutely complete conversion of the bromide to the sulphide by similar treatment, even at much higher temperatures, and the iodide resists conversion more obstinately than the bromide. Nor have we been able to find conditions under which the chloride may be converted while the bromide and iodide remain unattacked. In a study of the conditions best adapted to the reduction of silver salts electrolytically, we have obtained results which point to advantageous modifications of the methods heretofore known. We find that the treatment of the fused salts may be simplified, made more accurate, and extended to mixtures containing silver iodide.

In Kinnicutt's process the difficulties lie, first, in the impossibility of destroying the paper upon which the silver salts have been collected and washed, without affecting the reduction of the salts; secondly, in the obstinacy with which the spongy silver holds the sulphuric acid during washing; and thirdly, in the tendency of the chlorine liberated, when a chloride is present, to attack the electrodes.

Upon the first point nothing need be said; the difficulty is obvious and well known. As to the second source of error, our experience shows that rapid washing is not sufficient to remove the sulphuric acid included in the reduced silver, even when excessive amounts of wash-water are used; but that a considerable time is indispensable for the escape of the acid from the silver to the wash-water by diffusion. In several cases we have found errors, ranging from a single milligramme to six or seven, due to inclusion of the acid in residues which had been washed freely but rapidly, and which even after ignition, yielded slowly hot-water extracts, which gave the test for a sulphate by barium chloride.

The results of some experiment made to test the effect of the halogens set free in electrolysis are shown in the accompanying table:—

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* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. i., July, 1895.

Electrolyte 15 c.m.³ of H_2SO_4 (15 per cent) with the substance named.	Strength of current in ampères.	Time in hours.	Change in weight of the containing crucible.	Change in weight of wire electrode.	Connection of crucible.
			Grm.	Grm.	
1·7 grm. KI	0·46—0·25	24	0·0000	0·0000	Cathode
1 ,, KBr	0·50 0·18	35	0·0000	0·0000	Cathode
1 ,, KCl	0·48—0·18	26	0·0008 –	0·0001 –	Cathode
0·5 ,, HCl	—	—	*0·0009 –	0·0000	Cathode
0·5 ,, HCl	0·3	48	0·0004 –	0·0004 +	Anode

* Platinum tested for and found in solution.

So it appears that while neither bromine nor iodine attacked the platinum perceptibly under the conditions of the experiments, though set free in abundance, an appreciable amount of the metal did dissolve under the action of chlorine. Moreover, the solubility seems to depend chiefly upon the area of surface exposed, and not upon the electric polarity. The metal dissolved was re-precipitated by the action of the current only in the experiment in which, by reversing the direction of the current, and thus making the area of the anode large while that of the cathode was diminished, a corresponding increase of current density upon the cathode was brought about. It is obvious that, under ordinary conditions of electrolytic reduction, the solvent effect of the chlorine upon the platinum will naturally produce an apparent deficiency in the weight of silver reduced.

These sources of error in the electrolytic reduction of the fused silver salts we have endeavoured to overcome. The danger of change in the constitution of the salts during preparation for weighing we avoid by collecting them upon asbestos in a perforated crucible instead of upon paper; but in order to secure perfect electrical conductivity throughout the mass of silver salts subsequently collected, dried, and weighed, we place a disc of perforated platinum foil upon the prepared felt of asbestos. In this way perfect electrical contact is obtained, though the rapidity of filtration is somewhat impaired. The disc also serves the useful purpose of preventing the disturbance of the felt by the gas evolved from the walls of the crucible in the electrolytic process.* When the silver salts have been collected, washed, dried, and weighed, their fusion is effected by placing the capped crucible upon an anvil and directing the flame of a small blowpipe with care upon the mass from above. The anvil keeps the crucible cool, and tends to prevent the soaking of the asbestos with the fused silver salts, which would be disadvantageous in the washing process which follows the reduction. A rubber band, cut from rubber tubing of suitable diameter, is adjusted so as to cover the junction between the cap and crucible and make a water-tight electrolytic cell. When the electrolytic reduction is finished the band and cap are removed, the crucible is put upon the pump, the liquid is drawn through, and the precipitate washed in the usual manner.

It is obvious that the difficulty of washing out the sulphuric acid from the reduced silver may be avoided if it is possible to substitute for the sulphuric acid an electrolyte which, even if it were not easily removed by washing, should be volatile at gentle heat without affecting the silver; and the danger arising from free chlorine may be obviated by taking care to have the chlorine absorbed by the electrolyte as soon as it is liberated. We find that 25 per cent alcohol containing a tenth of its weight of oxalic acid meets all the conditions for the electrolytic reductions of the mixed chloride and bromide of silver. Such a solution, while possessing sufficient conductivity, absorbs the free chlorine to such an extent that, as we have found experimentally, no perceptible solvent action takes place upon the platinum, and nothing remains in the silver reduced under such a solution, which is not volatile at gentle heat without affecting the weight of the silver.

In the test-experiments recorded in the accompanying table known amounts of silver chloride and bromide were precipitated. collected, washed, dried at 150° C., and weighed in the filtering crucible, provided as usual with a layer of asbestos, which was in this case covered with the perforated platinum disc. The cap was put in place, the crucible set upon an anvil, and the salts fused with a blowpipe flame in the manner described. The rubber band was adjusted, the crucible nearly filled with the 10 per cent solution of oxalic acid in 25 per cent alcohol, and the current passed in the usual manner, the crucible serving as the negative electrode. When the reduction was judged to be complete the band and cap were removed, the crucible set upon the pump, and filtration of the liquid and washing of the residue carried out as usual. Finally the crucible, cap, and residue were ignited at a very low red-heat and weighed. The entire treatment was repeated until the constant weight of the residue showed that the reduction was complete.

AgCl taken.	AgBr taken.	Ag calculated.	Ag found.	Error.
Grm.	Grm.	Grm.	Grm.	Grm.
1·0608	—	0·7985	0·7990	0·0005 +
1·4380	—	1·0823	1·0823	0·0000
0·9998	—	0·7525	0·7522	0·0003 –
—	0·9959	0·5721	0·5723	0·0002 +
—	0·9979	0·5731	0·5732	0·0001 +
1·0044	0·4988	1·0426	1·0422	0·0004 –
0·4933	0·4966	0·6559	0·6568	0·0009 +

The manipulation of the method is very easy, and the results show that it is capable of yielding accurate results. The current ranged from 0·5 to 0·25 ampère, and for convenience the process was continued over night, though the reducton of amounts such as we treated is usually complete in six or seven hours.

Unfortunately this process, which works so well with the mixture of chloride and bromide, is not applicable to the reduction of silver iodide or to mixtures containing it. Experiment proved that the iodine set free in the electrolysis works over and over again upon the spongy silver, constantly regenerating silver iodide to a greater or less degree. As the result of many attempts to destroy the liberated iodine without inroducing anything objectionable into the solution, we finally settled upon a mixture made by neutralising two parts by volume of ordinary (40 per cent) acetic acid with ammonia, adding one part of ammonia, one part of alcohol, and one part of aldehyd (75 per cent). Such a solution we found to work very well on the whole, but as the reduction progresses it frequently happens that a deposit of white ammonium iodate forms upon the anode, which introduces too great resistance to the current. This deposit of iodate is, however, easily removed from the electrode by dipping it into hot water. Whenever the solution is so exhausted that free iodine begins to appear, the liquid should be carefully decanted and replaced by fresh; and before the operation is ended the decanted solutions and the washings of the electrode should be filtered through the crucible and the residue submitted again to the action of the current, to make it certain that loosened particles of silver or silver salt, possibly poured off or removed on the electrode, shall not be lost finally. The necessity of keeping the process under occasional supervision renders it undesirable to continue the action over night. In some cases of prolonged action without attention, we have noticed the formation of gummy carbonaceous matter, which could not be subsequently removed without the application of a degree of heat which might endanger the platinum in contact with the reduced silver. Many of the experiments recorded in the following table were completed within seven hours with a current not exceeding 0·5 ampère.

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* This device has been suggested by Puckner (*Journ. Am. Chem. Soc.*, 1893, 710) for holding down the asbestos in an ordinary filtration, and is no doubt of value when suitable asbestos is not at hand. A fairly good asbestos properly prepared, and deposited upon a perforated surface in which the holes are sufficiently numerous—best, as numerous as can be—does not. however, tend to rise during a filtration so long as the suction-dump is in action.—F. A. G.

AgCl taken. Grm.	AgBr taken. Grm.	AgI taken. Grm.	Ag calculated. Grm.	Ag found. Grm.	Error. Grm.
0·4779	—	—	0·3596	0·3591	0·0005 −
0·6096	—	—	0·4588	0·4591	0·0003 +
0·6774	—	—	0·5098	0·5099	0·0001 +
—	0·9969	—	0·5727	0·5726	0·0001 −
—	1·3703	—	0·7872	0·7875	0·0003 +
—	—	1·0613	0·4878	0·4877	0·0001 −
—	—	1·0621	0·4882	0·4875	0·0007 −
—	—	1·0140	0·4661	0·4662	0·0001 +
—	—	1·2012	0·5521	0·5530	0·0009 +
—	—	1·5031	0·6910	0·6914	0·0004 +
0·5035	0·4984	—	0·6653	0·6653	0·0000
1·0020	0·9998	—	1·3285	1·3283	0·0002 −
0·4939	—	0·6561	0·6734	0·6733	0·0001 −
—	0·5000	0·5304	0·5310	0·5316	0·0006 +

These results show that the process affords an accurate reduction of the chloride, bromide, and iodide of silver and mixtures of these salts. When the problem concerns the reduction of the chloride and bromide only, we give the preference to the reduction in alcoholic oxalic acid as being the simpler process. The latter process we have also applied succesfuly on a larger scale to the recovery of the silver in chloride residues.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 25th, 1895.

Mr. Walter Baily, Vice-President, in the Chair.

Prof. J. Perry read a paper by himself and Mr. H. F. **Hunt** on the "*Development of Arbitrary Functions.*"

During the discussion on Prof. Henrici's paper (April 13th, 1894), one of the authors described a graphical method of developing any arbitrary function in a series of other normal forms than sines and cosines, such as Bessels or zonal spherical harmonics. The method consisted in wrapping the curve which represents the function round a specially-shaped cylinder, not circular, and projecting this curve into a certain plane. Many months were wasted in finding with great exactness a sufficient number of co-ordinates of the trace of the cylinder suitable for a Zeroth Bessel development. The labour, however, was unnecessary, since the co-ordinate most troublesome to calculate is not really needed, the projection only taking place in one direction. To develop any arbitary function of x (say y) in normal forms, the real difficulty consists in finding the value of an integral, such as—

$$\int_0^a y \,.\, \mathrm{Q}\,(x) \,.\, d\,x\,;$$

where $\mathrm{Q}\,(x)$ is some tabulated function. If now, z is another tabulated function, which is the integral of $\mathrm{Q}\,(x)$, the required integral is—

$$\int y\, d\, z.$$

If the values for y for twenty-five equidistant values of x are known, from $x = o$ to $x = a$. Let the corresponding values of z be tabulated, and let a curve be drawn with the values of y as ordinates and the values of z as abscissæ; the area between the axis of z and this curve gives the value of the integral required. The authors give four tables containing the abscissæ for the four first terms in the development in Zeroth Bessels. They have tested the method by applying it to the calculation of a known function in terms of zonal spherical harmonics, and the agreement between the true value of the coefficients and those found is very satisfactory.

Prof. **Henrici** said the method was a new departure, since in the place of an instrument of complicated design, the authors only used a planimeter and pencil and paper, and obtained the same degree of accuracy. The fact that the series employed to test the method consisted of a finite number of terms seemed to him an objection. Prof. Carl Pearson had, in a recent conversation, informed him of a method for the development of functions which he (Prof. Pearson) had recently discovered. This method was not, however, so simple, at least in most cases, as that of the authors.

Prof. **Minchin** thought it would add to the intelligibility of the paper if it were stated that the method was similar to that employed when expanding in terms of a Fourier series or in spherical harmonics. In these cases you have a function which, when multiplied by other functions of different orders, kills all the terms except one. Graphic methods ought, in his opinion, to be very much oftener employed, and he considered that there was no problem in physical mathematics of which the solution could not be obtained by graphic methods. He would like to know if Prof. Perry had obtained a graphic method of calculating Bessels.

Mr. **Trotter** agreed with Prof. Minchin as to the neglect of graphic methods. He regretted that Prof. Perry did not continue to consider the method as the projection from a cylinder, as he had found the method of wrapping curves round a cylinder most useful.

Prof. **Perry**, in his reply, said he had adopted the expansion they had employed under the impression that the test was a particularly severe one. He had not discovered a graphic method of calculating Bessels. The reason they gave up the cylinder was the immense labour involved in calculating the y, co-ordinates of the trace, which would afterwards be of no use in the development of the function.

Mr. F. W. **Lanchester** read a paper on "*The Radial Cursor: a New Addition to the Slide-rule.*"

The ordinary form of slide-rule enables calculations to be made which involve multiplication and division; also involution and evolution where the indices are integers. The radial cursor allows of the solution of problems in which fractional indices occur; for example, in questions involving the adiabatic expansion of a gas, where an expression of the form $p\, v^{\gamma} =$ const. has to be dealt with, and where γ is not an integer, nor is it constant for all gases. In this case it is necessary to provide some ready means of dividing the scales on the rule and slider proportionally to the value of γ, which corresponds to the division and multiplication of the respective logarithms of the quantities dealt with in the proportion of the indices of p and v, *i.e.*, 1 and γ. This proportionate division of the scales is effected in the new cursor by a radial index-arm, which is arranged to swing about a stud fixed to a sliding bar running in guides at right-angles to the rule. All readings are taken at the points of intersection of a line on the radius arm and the edges of the slide. The distance of the pivot on which the radius-arm turns from the slide, and therefore the value of the index employed, is read off on a scale fixed to the transverse bar.

Mr. C. V. **Boys** said that owing to the kindness of the author he had been able to try the cursor and had found it of great service in dealing with questions of adiabatic expansion. The new addition to the slide rule suffers under the same disadvantage as the rule itself, namely, that a verbal or written description seems so very much more complex than is the actual operation when using the rule. The author's device might be described as an indiarubber slide-rule, for it performed the function of a slide-rule, in which the graduations of the slide were made on indiarubber, so that the ratio of the length of the scale on the rule to the length of the scale on the slide might be altered at will, and thus involution and evolution with fractional indices performed.

Mr. **Blakesley** asked how powers less than unity were dealt with.

Prof. S. P. **Thompson** and Mr. **Trotter** expressed their admiration for the author's method of "stretching" the scale.

Mr. **Burstall** said he had attempted to apply a similar method to the Fuller rule, but did not succeed, since in this rule there was only one scale. He hoped the author's method could be applied in a form such that a greater accuracy than 1 in 300 could be obtained.

Mr. **Bourne** thought the fact that the point of intersection of two lines inclined at an acute angle had to be read was likely to limit the accuracy.

The author having replied, the Society adjourned till November 8th.

NOTICES OF BOOKS.

A Laboratory Manual of Organic Chemistry; a Compendium of Laboratory Methods for the Use of Chemists, Physicians, and Pharmacists. By Dr. **Lassar-Cohn**, Professor of Chemistry in the University of Konigsberg. Translated, with the Author's sanction, from the Second German Edition by **Alexander Smith**, B.Sc., Ph.D., Assistant Professor of General Chemistry in the University of Chicago. Small 8vo, pp. 403. London and New York: Macmillan and Co. 1895.

The work before us is not one of those manuals of chemistry, organic or inorganic, which during the last few years have become almost painfully numerous. Dr. Alexander Smith is quite justified in saying that it "covers a field not previously occupied," and that it "does not take the place of any of the text-books of organic chemistry, but bears towards them the relation of an almost indispensable complement." It expounds the method used in the laboratory, whether in original research or in verifying results already obtained.

The work consists of two parts, a general and a special. The former treats of baths (for the regulation of temperatures); of crystallisation and dialysis; of decolourising liquids; of distillation, whether ordinary, fractionated, dry, or *in vacuo*; of drying; of extraction; filtration; of the determination of melting-points; of molecular weights; of work in sealed tubes; and of sublimation.

The special methods include condensation, the preparation of diazo-bodies of esters; fusion with caustic alkalis; the preparation of halogen compounds and of nitro-derivatives; oxidation; reduction; the preparation of salts; saponification; the preparation of sulphonic acids; and remarks on ultimate organic analysis. We note the remark that in the case of methylene-di-*p*-toluidine the Kjeldahl method gives the nitrogen 3 per cent too low, whilst the Will-Varrentrapp method gives a result in accordance with the theoretical composition.

We think that both teachers and students of organic chemistry will find this book a most satisfactory guide to research.

Quantitative Chemical Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By **Frank Clowes**, D.Sc., F.I.C., Professor of Chemistry in the University College, Nottingham, and J. **Bernard Coleman**, Assoc. Royal College of Science, Dublin, F.I.C., Head of Chemical Department, South-West London Polytechnic. Third Edition. Post 8vo, pp. 534. London: J. and A. Churchill. 1895.

The work of Messrs. Clowes and Coleman has evidently given satisfaction to teachers and students, since a third edition is already required. It is admittedly an improvement on its two predecessors, having been again enlarged and enriched with new methods of determination. Additional figures have been introduced for the sake of clearness, and the table of contents has the valuable feature of giving references both to paragraphs and pages.

The bibliography of analytical works will be found of value not merely to students, but even to experienced practitioners.

Part I. treats ably and thoroughly of general and preliminary operations.

Part II. instructs in gravimetric analysis, the various methods being placed in the order of their increasing difficulty.

Part III. treats of the volumetric analysis of liquids.

In Part IV. we find accounts of more complex determinations, both gravimetric, volumetric, and of a mixed character. Here are included the analysis of ores, of important industrial products, waters, foods, and various organic substances.

The simple methods of gas analysis are described in Part V.

The only electrolytic method is that described for the determination of copper.

Upon spectroscopic quantitative analysis the authors do not enter. Methods for the determination of the metals of the so-called rare earths have not been inserted. In the appendix we find what may be called typical results of analyses.

There are also a series of tables of constants for calculating the results of analyses. These, however, seem to us by no means preferable to the tables given in "Rose's Quantitative Analysis," though many of the latter require re-calculating, on account of the more accurate determinations of atomic weights made since 1849.

On the subjects which it includes the work before us is an excellent guide.

The Forces of Nature; a Study of Natural Phenomena. By **Herbert B. Harrop** and **Louis A. Wallis.** Pp. 160. Columbus, Ohio, U.S.A.: Harrop and Wallis. 1895.

The work before us is a necessarily sketchy survey of the phenomena of the universe, intended, not for the student, general or special, but for the general reader who is desirous of a better acquaintance with the *cosmos* which he inhabits.

In successive chapters, they consider the solar system, the earth, the atmosphere, and sound, chemistry (with the structure of matter), radiant energy, light, heat, and actinism, electricity and magnetism.

The second part consists of what the authors term "disconnected essays and paragraphs on scientific questions." such as the nebular hypothesis, spontaneous combustion, spontaneous generation, argon and helium, and scientific theories in general.

In most instances the authors may be accepted as trustworthy guides; but in speaking of the doctrine of abiogenesis, they overlook the capital part taken in its refutation by the illustrious French philosopher whom the world has just lost. They accept Huxley's prophecy that, in the future, protoplasm will be formed artificially from its lifeless elements. They are believers in the nebular hypothesis and in organic evolution. On the great question of chemistry, whether the elements are absolutely primordial and inconvertible they give no certain sound. They consider the "canals" on the surface of Mars as artificial. The description of snow as rain frozen is much more applicable to hail.

The explanation given of "hypothesis" as a guess having no material foundation cannot be accepted. Most of all must we hesitate at the bold assertion that the simple laws of mechanics govern "the complicated functions of organic life."

We perceive that the authors announce a companion volume on the "Forces of Life," including the evidences of organic evolution.

Examination of Water for Sanitary and Technic Purposes. By Henry Leffmann, A.M., M.D., Ph.D. Third Edition, Revised and Enlarged. With Illustrations. Philadelphia: P. Blakiston, Son, and Co. 1895.

The author classifies waters as rain-water, surface-water, subsoil-water, and deep water; the latter being chiefly that obtained from Artesian wells. The instructions concerning taking samples of waters and their analytical examination do not differ essentially from those to be met with in other manuals of the same kind. The instructions for the determination of saline and organic ammonia (known respectively as "free" and "albumenoid" ammonia) are substantially those given by Wanklyn. The Kjeldahl process is described with the remark that it was first successfully applied in water analysis by Drown and Martin. Concerning the Frankland and Armstrong process we read that, "it requires complex and expensive apparatus and special skill, has been shown also to be liable to inaccuracies, and has not come into general use."

For the determination of the nitrogen present as nitrates, the author recommends Ilosway's modification of the Griess process. The oxygen-consuming power of a water may be determined by Tidy's method, modified by Dupré, and for the oxygen existing in solution that of Blarez is proposed.

For the determination of phosphates—a point deemed unessential by many chemists, including Wanklyn—Dr. Leffmann tests with molybdenum solution. We are glad to find that among the poisonous metals chromium is not overlooked—a dangerous impurity which may possibly occur in industrial localities. We can scarcely accept the view that Beggiatoa—commonly called "sewage fungus"—indicates suspended organic matter. It occurs in deep springs charged with sulphur and in sulphuretted industrial waste waters not charged with organic matter.

The author enters to some extent upon the presence, detection, and possible effects of micro-organisms; a subject overlooked in the earlier manuals of water analysis, but upon which biologists and chemists have not yet come to a full and clear agreement.

The work before us is, however, one which the sanitary chemist may with some advantage include in his library of reference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 16, October 14, 1895.

The perpetual Secretary read a letter signed by the Duc de la Broglie, of the French Academy, Leopold Delisle, of the Academy of Inscriptions and Literature, Ch. Harmite, of the Academy of Sciences, Ambroise Thomas, of the Academy of the Fine Arts, and G. Picot, of the Academy of Moral and Political Sciences, inviting the members to be present at a religious ceremony to be celebrated on October 23rd in the Church of St. Germain des Prés in memory of those of the members who have died since the foundation of the Institute. The service will be conducted by the Bishop of Autun.

The President announced the death of Baron Larry, a "free member," which took place on October 8th. Emile Blanchard took occasion to claim for Baron Larry the honour of having been the advocate of conservative surgery.

Determination of Argon.—Th. Schlœsing, jun.—(See p. 211).

Action of Hydrochloric Acid upon Copper.—R. Engel.—The decomposition of hydrochloric acid by copper with the liberation of hydrogen is so slow and so inconspicuous that it has been often overlooked. This acid, in a solution saturated at 15°, is decomposed by copper so rapidly that the liberation of hydrogen may be shown in a lecture. If a little platinum chloride is added to the acid the reaction becomes tumultuous, but soon slackens, so as to be almost imperceptible, though it continues for several years. The decomposition of the hydrochloric acid by copper ceases when the solution contains less than 48·8 to 49 milli-mols. of HCl. Such a solution has a sp. gr. of 1·083 and the composition $HCl+10H_2O$. The action becomes extremely slow when the liquid is saturated with cuprous chloride. If we pass a current of gaseous hydrochloric acid into water in presence of copper and cuprous chloride the action is rapid. Anhydrous hydrochloric acid is always decomposed by copper.

Action of Potassa and Potassium Ethylate upon Benzoquinone.—Ch. Astre.—The author has isolated a compound formed by the union of 2 mols. of alcohol and 1 mol. of bipotassic quinone. This derivative is interesting as being formed in presence of an excess of potassa, which seems to indicate that benzoquinone contains only 2 atoms of hydrogen capable of being replaced by potassium.

Combinations of Antipyrin with the Diphenols; Influence of the respective Positions of the Hydroxyls.—G. Patein and E. Dufau.—The diphenols, pyrocatechin, resorcin, and hydroquinone behave in different manners with antipyrin. The ortho- and para-diphenols combine with two mols., but the meta- with one only. The fixation is effected upon one of the atoms of nitrogen by the intervention of phenolic hydroxyl, which loses this property in proportion as its hydrogen is replaced by a metal or a radicle.

Zeitschrift fur Anorganische Chemie.
Vol. viii., Part 3.

A Contribution to the Constitution of Inorganic Compounds.—Alfred Werner (Second Communication).—This valuable paper requires the eight accompanying figures. We can merely remark that it is mainly of a controversial character, with especial reference to the recent memoir of Jörgensen on the bases of cobalt, chrome, and rhodium.

A further paper, by the same author, discusses the relation between the co-ordination and valence compounds. It is laid down that the fundamental law regulating the formation of these elements is the effort of the central element to group around itself four radicles.

Atomic Weight of Tungsten.—Mary E. Pennington and E. F. Smith.—The mean value obtained from nine determinations is = 184·921, the maximum result having been 184·943, and the minimum 184·900. The details of the experiments have appeared in the *American Chemical Journal.*

In another paper on the same subject, by E. F. Smith and E. D. Desi, the mean atomic weight of tungsten is given = 184·704.

Specific Heat of Metallic Tungsten.—A. W. Grodspeed and E. F. Smith.—The authors give the value = 6·25, taking the atomic weight of tungsten as 184·921, or = 6·243, on the basis of Smith and Dasi's atomic weight.

Double Transposition of Gaseous Bodies.—Henryk Arctowski.—This paper (a translation from the French—or Flemish?) requires the two accompanying figures. The law laid down is an extension of that of

Berthelot—"If the mixture of the vapours of two compound bodies can give on double decomposition a product solid at the prevailing temperature and pressure, whilst the three other products remain gaseous, this will always solidify in a solid form outside of this atmosphere."

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 116.

Review of Improvements recently introduced in the Industry of Distillation.—L. Lindet.—This bulky memoir does not admit of useful insertion, the rather as the improvements concerned largely relate to the manufacture of a spirit from beet-root.

Review of the Progress recently effected in the Milling Industry.—M. Colson Blanche.—We are surprised at finding the production of meals and flour classed among the "chemical" industries.

MEETINGS FOR THE WEEK.

Monday, 4th,—Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "Filtration of Sewage Effluent," by W. J. Dibdin, F.I.C., F.C.S.
Wednesday, 6th.—Society of Public Analysts, 8. "Note on the Bromine and Iodine Absorptions of Linseed Oil," by Rowland Williams. "The Determination of Oxygen in Commercial Copper," by Bertram Blount. "Note on a Recent Milk Case involving an example of Abnormal Milk" and "Note on 'Filled Cheese,'" by R. Bodmer. "The Composition of Condensed Milk," by Messrs. Pearmain and Moor. "Note on the Composition of Commercial Condensed Milk," by A. H. Allen. "Note on the Estimation of minute quantities of Metals in Liquids" and "Note on a Convenient Form of Polarimeter for Examining Essential Oils," by Messrs. Budden and Hardy. "Note on a series of Analyses of a Private Water Supply," by E. Russell Budden.
Thursday, 7th.—Chemical, 8. "The Temperatures of Flames and the Acetylene Theory of Luminosity," by Prof. Smithells. "The Action of Acidic Oxides on Salts of Hydroxy-acids," by Prof. G. G. Henderson and D. Prentice. "Sodium Nitrososulphate, and the Constitution of Nitrososulphates," by Profs. Divers and Haga. And other papers.
Friday, 8th.—Physical, 5. "The Magnetic Field of any Cylindrical or Plane Coil," by Mr. Everett. "The Latent Heat of Volatilisation of Benzene," by Mr. Griffiths and Miss Marshall. "The Comparison of Latent Heats of Volatilisation," by Prof. Ramsay and Miss Marshall.

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THE CHEMICAL NEWS.

Vol. LXXII., No. 1876.

BRITISH ASSOCIATION.

Ipswich Meeting.

Sections A and B (Joint Meeting).

*Discussion** on Argon *and* Helium.

The first item on the agenda was a paper by Lord Rayleigh, Sec. R.S., "*On the Refraction and Viscosity of Argon and Helium.*" His lordship stated that what he had to bring forward consisted of little more than certain measurements of the physical properties of these gases. With regard to argon, he might say that the gas he used was prepared from air, at the Royal Institution in London, by what he might call the oxygen method—that was to say, the nitrogen of the ordinary air was removed by the aid of oxygen and with a series of electric sparks. As the proportion of argon in the air, however, was so small—only 1 per cent—the process of separation was extremely slow and tedious. By means of an electric arc, kept up for several weeks in a mixture of oxygen and atmospheric nitrogen, he finally obtained more than 3 litres of argon at atmospheric pressure. Having done this, his primary object was to weigh the gas on the same scale that other gases had been previously weighed, in order to see whether the gas prepared by the oxygen method had the same density as gas prepared by the magnesium method. He might say at once that the density proved to be exactly the same. The other physical properties that remained available for measurement were the refractive index and the viscosity. The refractive index was measured by the interference method. The eyepiece was constructed of cylindrical lenses. To avoid the use of cross-wires, the tubes containing the gases under comparison were arranged so as not to occupy the whole field of view, some light passing parallel to and outside them; two sets of fringes were thus obtained, which could be brought to coincidence by varying the pressure of either gas. Adjustments were made for several pressures, one of the tubes always containing air. The refractive index of argon proved to be 0·961, only about 4 per cent less than that of air.

The next question arose as to the corresponding property of helium. For this purpose he used gas which Professor Ramsay had separated from clèveite, and he was astonished to find that the refractive index of this gas was as low as 0·146. Dry air was in both instances taken as the standard, so that the refraction of helium was about one-seventh part only of that of the air. It might be that at the present time a precisely accurate value of the physical properties of these gases was not of much consequence; but if it should be proved, as was probably the case, that either or both of these gases were mixtures, then a precise knowledge of these properties would be of the utmost importance. The refraction of helium was far below that of any known gas.

The other property that he took up was the viscosity of these gases. By viscosity one meant the force that was called into play when one layer of gas tended to slide upon another; in practice viscosity was usually measured by the rate at which the gas or the liquid could be caused to flow through a very fine capillary tube. There were some difficulties attending this experiment, which he explained, but the results were not very importantly affected. To put the matter shortly, and again taking dry air as the standard, he found that the viscosity of argon was 1·21, and of helium 0·96. These figures, though less striking than those referring to the refractive index, threw some light nevertheless upon the character of the gases. If they compared oxygen and air, they would find that the ratio was 1·11, oxygen being the most viscous gas previously known; but the figures he had just given showed that argon was more viscous than oxygen, and therefore stood at the head of the list of viscous gases. He hoped that some other members present would point out the chemical conclusions that were to be drawn from these facts.

There was one other point that he should like to mention. Some time last year—in fact almost immediately after Professor Ramsay and himself had established the existence of argon—they obtained, with the assistance of Dr. Arthur Richardson, some gas from the Bath spring which had hitherto been supposed to be nitrogen. At that time he thought that this gas might prove to be in large degree composed of argon. That anticipation was not verified. When the Bath gas was treated in the same way that atmospheric air was treated, in order to isolate what was supposed to be pure nitrogen, it was found that the weight of nitrogen so obtained was not so great as the weight of nitrogen obtained from the atmosphere. The conclusion was that the Bath gas contained less argon than might have been expected; and this rather puzzled him, because argon was more soluble in water than nitrogen. The matter rested for a while, until, in the course of the spring, Dr. Ramsay isolated helium, and found that its density was exceedingly low—only about double that of hydrogen. So far as was yet known, the chemical properties, or want of chemical properties, of argon and helium were about the same, so that any process by which argon was separated, either from air or from the gas of mineral springs, would also separate helium. It was then suggested that the fact which had puzzled them with regard to the Bath gas was explained by the presence of helium, which had obscured by its abnormal lightness the extra density of argon; and he had since ascertained by spectrum analysis that, as a matter of fact, the Bath gas did contain helium. (Applause.)

Dr. J. H. Gladstone, F.R.S., who was received with applause, next read a paper on "*Specific Refraction and the Periodic Law, with reference to Argon and other Elements.*" In doing so, he said that in 1869, 1877, and 1883, he had shown that the specific refractive energy of the metallic elements was usually in the inverse order of their combining proportions, and that the specific refractive energies of the elements in general were to a certain extent a periodic function of their atomic weights. The present communication referred to some developments of these old observations. With regard to (1) argon, the specific refractive energy of argon gas, as reckoned from Lord Rayleigh's data, is 0·158. Deeley suggested that this might throw light upon the question whether the atomic weight is 19·94 or double. If the atomic weight be 19·94 the molecular refraction will be 3·15. This figure is almost identical with that belonging to oxygen and nitrogen gas. Taking the specific refractive energy of the elements with atomic weights between 12 and 23, including argon, as 20; viz., carbon 0·417, nitrogen 0·236, oxygen 0·194, fluorine 0·03, argon 0·158, sodium 0·209; argon appears in place on the rise after the great descent from carbon to fluorine. On the other hand, it would seem to be out of place in the neighbourhood of calcium, which has a molecular refraction of 10·0, and a specific refractive energy of 0·248. (2) The fact that the specific refractive energies of the univalent metals are generally inversely as the square root of their atomic weights is confirmed by further research, the product of the two being about 1·3. The same was shown to hold good of the earthy metals in the second column of Mendeléeff's table, the products in that case being fully 1·4. The rule does not apply to the halogens in column VII. As to column VIII., iron, palladium, platinum, and gold all give products

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* For portions of this Report we are indebted to the *East Anglian Times*. Proofs have been sent to each speaker for correction.

which are far higher. This confirms the belief that gold is not rightly placed in column I. (3) It is known that the refraction of a salt when dissolved in water is often slightly modified by the proportional amount of the solvent. The author said that he and Mr. Hibbert had recently found that salts of the metallic elements, in columns I. and II. of Mendeléeff's table, showed generally an increased refraction on dilution, those of metals in column VIII. a diminished refraction.

Professor Schuster, F.R.S., then opened a discussion "*On the Evidence to be gathered as to the simple or compound character of a Gas from the Constitution of its Spectrum.*" The purpose they had in introducing this subject, he said, was to inquire whether they could, from the spectrum of a body, draw any conclusions as to the probable nature of the gas, as to whether it was compound or simple, or as to the group of chemical elements to which it belonged. It might appear at first sight that spectroscopists ought by this time to be able to draw some definite conclusions upon these points; but, in order to show the very great difficulties with which they had to contend, he would draw attention to the analogous case—taking the vibrations of sound instead of those of light. If an organ pipe were examined it would be a pretty easy thing to calculate and to learn what different tones that pipe would emit. Supposing, however, that they were outside a room in which bells were placed, possibly half-a-dozen, and that they were asked, simply from the sound of those bells, to conclude how many bells there were, and what was their shape, and the constituents used in making them, then they would be face to face with a problem exceedingly difficult, if not incapable, of solution. It was a difficulty of this kind in which they were placed in regard to the spectrum. He would not go so far as to say that every element behaved differently; but they certainly did not always behave exactly alike, and any conclusions that might at present be drawn from the spectrum of a body must therefore be exceedingly uncertain. Dealing at considerable length with somewhat abstruse facts and theories, the first points presented for consideration were these:—What is it that vibrates in a body which sends out rays and vibrations of light, and how is it possible that bodies which are called monatomic—like mercury vapour, for instance—could show not only a simple vibration of a definite period, but a great multiplicity of lines and a very complicated spectrum? The learned Professor considered that discussion was not likely to be productive of much useful result, simply because they had at present so little knowledge of the facts. His conclusions were that they required in the first place an accurate mapping of the spectra of compound bodies, and some kind of mathematical theory as to the very curious distribution of the wave lengths of both the bands and the lines revealed by the spectrum.

The despondent view of Prof. Schuster was not shared by Prof. Runge, of Hanover, who at this point contributed an account of the researches of himself and Prof. Paschen on the spectrum of clèveite gas—undoubtedly the most complete analysis of spectra hitherto made—proving that helium is not a simple element, but consists of two, and not more than two elements. They had proved that the spectrum of clèveite gas consists of two systems, each with three series of lines, six in all; the two systems can be distinguished by the fact that one of them consists of double, the other of single, lines. Prof. Runge described the method of diffusion by which he and Prof. Paschen have altered the relative intensities of the lines in these two systems. They find that the double-line substance, which gives the line D_3, and ought therefore alone to be called helium, is always present in the sun's chromosphere, and diffuses more slowly than the single-line substance. The lattter substance only occurs in spectra of the sun's chromosphere about once in four observations. As he resumed his seat, the young Professor, whose work in this department is well known to those most deeply interested, was loudly cheered.

Lord Rayleigh said the audience had already shown their appreciation of the remarkable results that Professor Runge had put before them with such great lucidity, speaking almost as freely as though he had been speaking in his native tongue. (Applause). There could be no doubt that these results were of the highest order of interest. He was not himself an expert in spectroscopic matters; those who were would tell them that there was little work which could be compared in precision and value with that which had now been put before the meeting. The strong evidence given them as to the compound character of the gas from clèveite was a point of the utmost interest. He (Lord Rayleigh) had supposed that the probabilities were not against such a conclusion. The gas was almost of unknown origin; the chemical character of it was unknown, and the manner in which it was held in the mineral was still entirely a matter of speculation. Its division into two elements, and the fact that there were no indications of more than two, seemed to be a point very well made out, so far as one could expect in matters of this kind. He did not know whether Professor Runge could tell them anything of the same sort about argon—whether he had any presumptions from the spectra as to the character of the element or elements it might contain. Without going further, he would leave the consideration of the matter in more competent hands.

Dr. G. Johnstone Stoney, F.R.S., said that his admiration of the splendid piece of work which had been carried on by Prof. Runge and his colleague, dated from the original publication of the results of their investigation some six weeks ago. Then he was so deeply impressed with its importance, in the present position of the investigations with reference to these elements, that he at once wrote to the editors of the *Philosophical Magazine*, and they had inserted a translation (*Phil. Mag.*, Sept., 1895) of the principal memoir for the better information of residents on this side of the German Ocean. Dr. Stoney was just touching upon the paper he had to read, when Prof. Lodge made a private communication to him. Turning aside for the moment, Dr. Stoney said it would be very advisable at that juncture to call attention to the unfortunate position in which scientific investigation in the British Islands stood in comparison with that of at least one other country in Europe. There was no scientific man in these Islands who possessed a laboratory furnished with the appliances for carrying on such investigations as those which had just been placed before the meeting. Their knowledge of the subject was therefore in a somewhat correspondingly backward position. This was a difficulty for which a remedy should, he thought, be found as soon as possible. An apparatus which would measure the half or the third of a tenth metre would really do nothing in an investigation of this kind; they must procure apparatus, like the splendid apparatus in Hanover, which would measure to the fiftieth part of a tenth metre with certainty.

Dr. Armstrong (intervening) said he should like, on behalf of the chemists, who had not said anything up to that time, to express the universal admiration which they must all have of the communications just made to the meeting. He had risen at that juncture not merely with the object of saying this, but also in order to correct the impression which Dr. Johnstone Stoney had just endeavoured to make, at the instigation of Professor Lodge, that they were not capable of doing this kind of work in the British Isles.

Professor Lodge—It was not my instigation. I was just reminding Dr. Stoney of something that I knew, from what he said to me last night, he was anxious not to forget to say. (Laughter).

Dr. Armstrong—And that happens to agree rather curiously with your particular views. (Renewed laughter). The Doctor went on to say that this work had been done in Hanover by individual effort, after the fashion usual in England. If the idea of making such investigations as these occurred to men in this country, who had the requisite capacity for undertaking them, he was sure that the effort would always be made.

Dr. JOHNSTONE STONEY then read his paper on "*The Interpretation of Linear Spectra.*" The abstract of his argument was as follows:—

In most of the spectra that consist of lines, very remarkable groups present themselves, in which the lines are seen to be associated into definite series. In such cases, except under special circumstances, we may safely presume that all the lines of a group arise from the motion of a single electron in each molecule of the gas. Very striking examples of such groups are present in the absorption-spectrum of oxygen and in the bright line spectrum of carbon. The oxygen of the earth's atmosphere produces the great A group of double lines in the solar spectrum, as well as the very similar great B group, and the α group. It also produces a group more refrangible than D, about which we know less. This group is much fainter than the others, and it is only under exceptional circumstances that it can be seen at all in the solar spectrum. Each of the other three groups can be distinguished into two sub-groups; which from their appearance have been called a head and a train. The general features of these three groups are the same, and Mr. Higgs has made a careful geometrical analysis of one of them, the great B group (*Proceedings of the Royal Society*, March, 1893, p. 200). From his analysis we may infer that the head and the train are due to motions in the molecules which are distinct, although related to one another. This conclusion receives further support from the circumstance, that in the double lines of "the head," it is the violet component of each pair which is the stronger; while in the train it is the red component of each pair which is the stronger. In a paper in the *Scientific Transactions of the Royal Dublin Society* for 1891, p. 563, the present author pointed out that if we proceed on the probable supposition that the motion of each electron is an orbit of some kind going on within the molecules, it can be shown that the partials of the motion of the electron which causes the lines are elliptic partials, and that where an elliptic partial suffers an apsidal perturbation, it divides into two circular sub-partials, giving rise to the two constituents of a double line. We may infer from this that the sub-partials corresponding to the red constituents of the fourteen or more double lines of the train of B are circular motions revolving one way, and that all the violet constituents of these double lines result from circular motions revolving the other way. In order to advance beyond this point, it is necessary to make two further hypotheses which probably are both true. Two hypotheses must here be ventured upon, because observations with the spectroscope give us no information as to the phases of the elliptic partials or the planes in which they lie. One hypothesis that recommends itself is that the circular sub-partials belonging to a connected series of double lines, *e.g.*, to the train of the great B group, lie in one plane. Another hypothesis which we may venture to make, as a preliminary working hypothesis, is that the amplitude of the motion of the electron has its maximum value at starting, *i.e.*, when that event has occurred at the close of a struggle between two molecules which has set up that motion of the electron which continues during the comparative repose of the quiet, undisturbed journey in which the molecule is indulged after its encounter. With these assumptions it is possible to synthesise all the motions causing the red constituents of the double lines into one motion, which is, however, not circular, but a slowly contracting spiral; and a similar resultant spiral motion turning the opposite way is furnished by the sub-partials forming the violet constituents. While these spirals are being traversed, the radii or semi-amplitudes of the circular motions of which they are composed, and which correspond to the individual lines in the spectrum, are becoming shorter or longer, owing to the escape of energy to the ether or absorption of energy from it; so that the actual orbits are spirals lying somewhat inside or somewhat outside those which result from the assumption that the radii retain their length. These two spiral motions combine at each instant into a single elliptic motion so elongated that it is nearly a linear vibration, and this elliptic motion continues to represent what occurs, if subjected to the five following perturbations:—

1. A decrease of amplitude.
2. A diminution of periodic time.
3. A slow apsidal motion in a direction opposite to that in which the revolution of the electron in the orbit takes place.
4. A slight fluttering motion which may be represented by a very shallow wave running rapidly round the ellipse.
5. A further slight modification of the form of the ellipse which takes the form of a secular perturbation.

Accordingly we arrive at the conclusion that an elliptic motion undergoing these perturbations is such a motion of an electron as would produce the entire series of lines in the train of B. A similar motion would produce the train of A, of α, and of each of the other similar groups, if such exist in the spectrum of oxygen. These elliptic motions undergoing perturbations may be appropriately called mega-partials in their relation to the actual orbit described in oxygen by the electron that produces all these trains of lines, since that orbit is the resultant which we should get by superposing the motions in these few mega-partials. A similar treatment applied to "the head" of any of the oxygen groups shows that it, too, arises from an elliptic motion subject to perturbations, the chief differences being in the law connecting the falling-off of amplitude and the periodic time, and that the quick fluttering perturbation is absent; also that the apsidal motion takes place in the opposite direction. In oxygen, the strength of the lines of each sub-group fades out towards the red. When the fading is in this direction, it can be shown that the periodic time decreases as the amplitude falls off. Where, as in the carbon groups, the lines fade out towards the violet, the periodic time becomes longer as the amplitude decreases. And, finally, if the lines present themselves, when plotted on a map of oscillation frequencies, as disposed symmetrically on either side of a common centre, this indicates that the periodic time continues unchanged during the shortening of the amplitude. This suggests the cause of the width of spectral lines in general, so far as their width is not merely apparent, *i.e.*, due to the Doppler effect of the translational motions of the molecules, or to the breadth of the slit of the spectroscope. The rest of the width of the line, as seen, is its true physical width, and seems to be due to the interchange of energy between the molecule and the ether. This leads to diminished amplitude; and this reduction of the amplitude may be accompanied by either a reduction, or an increase, or a persistence unaltered of the periodic time; according to the way in which the motion of the electron is dynamically associated with the rest of the events which go on within the molecule. If the periodic time decreases, this gives rise to a ruling fading out towards the red; if there be an increase of the periodic time, the shading is towards the violet; while if the line fades out both ways symmetrically, there is no change in the periodic time. The relative intensities and the spacings of the lines of the ruling depends on the law which connects the escape of energy, and the shortening of the semi-amplitude; and in its turn this law depends on the dynamical relations in which the parts of the molecule stand to one another. The excessively fine rulings of which the widths of individual lines consist, can probably not be seen otherwise than as a shading, unless perhaps in some very few exceptional instances, owing to their being blurred together by the Doppler effect. We have attributed these very fine rulings to the interchange of energy with the ether. On the other hand, the more conspicuous rulings, such as those we have been studying in oxygen and carbon, seem to be associated with the transference of energy from one motion within the molecule to another. This may be briefly described by saying that the widths of the individual lines and their being in various ways shaded off, are due to radiation, while that they are arranged in series is due to conduction.

A Discussion followed (the audience having by this time become very thin), the speakers including Professor Liveing, Lord Kelvin, Professor Fitzgerald, and Dr. Macfarlane Gray. Two or three papers on "Orthochromatic Photography" were held over to a later meeting, probably in the Chemistry Section.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 216).

On the Coal-Gas.—When the air is pure, coal-gas taken direct from the main burns in a Bunsen burner, or blowpipe, or blowpipe fed with air or oxygen, without showing a trace of the sodium line on spectroscopic examination. During my examination of the coal-gas spectrum, I tried whether the presence of compounds of ammonia or cyanogen modified it. With this view I examined the spectrum of oxy-coal-gas, made with gas either taken direct from the main or kept in a gasometer where it was stored, having been previously deprived of compounds of ammonia and cyanogen by its passage through flasks filled with broken pumice-stone, and moistened respectively with a strong solution of caustic potash and sulphuric acid diluted with its volume of water. I have never detected any difference between the spectrum shown by ordinary gas and that by the gas purified as above.

With the object of economising oxyhydrogen-gas as much as possible, on account of the difficulty of preparing hydrogen fulfilling all requirements, I often used oxy-coal-gas to eliminate, from compounds, the sodium which is accidentally contained in them. I also used the oxy-coal-gas blowpipe, which is very much easier to manipulate, to check the results given by the oxyhydrogen burner. These requirements led me to examine the oxy-coal-gas jet formed from coal-gas under pressures respectively of *four* and *five* c.m. of water. The results having been the same, I shall limit myself to mentioning here those obtained under constant pressure of *four* c.m. of water.

When the internal surfaces of the service-pipe and burner were thoroughly moistened, the gas-jet issuing from a platinum burner, with a hole 1 m.m. diameter, formed a luminous flame 25 c.m. high and 1½ c.m. diameter. When the supply of oxygen was regulated so that *all luminosity* disappeared from the flame, its height was reduced to 17 c.m. and its diameter to 7 or 8 m.m.

In pure air this flame is deep pure blue, *without an inner cone;* spectrum analysis of it shows an absolutely *dark* spectrum. On gradually increasing the supply of oxygen, the colour intensity of the flame decreases and the light intensity increases; instead of deep blue it becomes *sky-blue.* It develops at the same time a highly luminous inner cone, pure light blue in the absence of sodium, and pale blue tinged with green whenever it has the least trace of sodium in it. Spectrum analysis of the sky-blue flame and of the inner cone reveals a hydrocarbon spectrum. I found that the *luminous intensity was greatest* and *the spectrum most complete* when the inner cone was reduced from its original height of 9 or 10 c.m. to about 5 c.m. Whatever the height of the inner cone might be, the *appearance* of its spectrum is the same; it consists of six well-marked bands, shaded from left to right: *one* reddish-brown band, *two* bands of different shades of green, and three pure blue bands. The bands are defined by lines, the number of which varies with the luminous intensity of the cone. With maximum intensity, examining *the apex or one side of the cone*, the bands are made up as follows:—

1. The red band—composed of four sharp very bright lines, situated between 43 and 49 on the micrometer of my Steinheil spectroscope. Farther on I shall give its value as a function of Fraünhofer's "A, B, C, D, E, *b*, F, G, H" lines.*
2. The first green band—composed of four sharp very bright lines, situated between 56 and 66 on the same micrometer.
3. The second green band—composed of three very bright lines, situated between 72 and 77 on the same micrometer.
4. The first blue band—composed of five sharp lines, less bright, situated between 90 and 96 on the micrometer.
5. The second blue band—composed of four faint lines, situated between 113 and 115 on the micrometer.
6. The third blue band—nebulous and very faint, extending from 117 to 118 on the micrometer.

When the luminous intensity was not at its maximum, but yet the bands were broken up into quite distinct lines, the second *green* band consisted of only two lines and the first blue band of only four lines, instead of three and five lines respectively.

The coal-gas spectrum generally recognised appears then to be an *incomplete* spectrum. The connection between the number of lines in the coal-gas spectrum and its luminous intensity is undoubted, and the influence of a rise of temperature on them both seems to me indisputable.

I made a set of experiments to ascertain what influence the lines in the coal-gas spectrum had on the spectra I was studying under different conditions, and I found out definitely that the spectrum of sodium, potassium, thallium, lithium, calcium, strontium, and barium is *the same* when rendered incandescent either in an *oxyhydrogen* or *oxy-coal-gas* blowpipe. Having obtained the coal-gas spectrum, it suffices to place a compound of sodium, potassium, thallium, lithium, calcium, strontium, or barium in the desired part of the jet, in order to extinguish completely all lines in the coal-gas spectrum, and replace its characteristic bands and lines by the lines of each of these metals.† Doubt is only possible in the case of the green lines shown at a very high temperature by barium compounds. This metal itself has a band made of very fine green lines, as observed by M. Bunsen, that might be mistaken for the green lines in the coal-gas spectrum. I shall be more

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* I refrain from giving the exact position of each band and line in the coal-gas spectrum, because in many cases the limit of error in assigning the position is greater than the distance between two adjacent lines.

† I call the *appearance* of the coal-gas spectrum the *visibility* of the characteristic lines and bands seen during spectrum analysis of the inner cone of an oxy-coal-gas blowpipe, and in the same way I designate by the term *extinction* the *non-visibility* of lines of bands *previously* seen. I hold that a spectrum formed of lines and bands can exist in the background of the spectrum without being visible to the sharpest eye. Thus, when one makes, by means of a spectroscope of low absorption power, and fitted with a micrometer with a luminous scale, a spectroscopic examination of a *short* induction spark without a condenser, between two platinum points, in air *free from sodium*, and when one refrains from illuminating the spectrum, one *always* sees a spectrum of atmospheric lines and bands on an *absolutely dark* background. By then illuminating the spectrum, whether by coal-gas or by the radiation from an incandescent platinum ball, one instantly masks the spectrum of the atmospheric bands and lines; the eye ceases to see them. The bands and lines are in this case replaced by a *continuous spectrum*, the intensity of which is in proportion, at the same time, to the intensity of the spectrum of the atmospheric lines and to the intensity of the source of light. The observer can at pleasure, and without limit as to the number of repetitions, cause to appear or disappear the two kinds of phenomena. During the revision of my spectroscopic studies with Prof. Depaire, we frequently had occasion to verify the perfect truth of the facts stated above, and we convinced ourselves that it was not possible to obtain by spectrum analysis, even of a short induction spark without a condenser, a spectrum free from atmospheric lines and bands, when we refrained from lighting the micrometer with a luminous scale. The light from the micrometer, whilst extinguishing the spectrum of the atmospheric lines, always replaced it either by diffused light or by a more or less well-defined *continuous* spectrum. *In my opinion it is proved to be impossible to obtain a spark spectrum without atmospheric lines and bands when the background is* DARK.

explicit on this point when I describe the results of my studies on these last compounds.

The rays from the metallic compounds I have just mentioned extinguish—that is, render invisible—the rays from coal-gas burning in oxygen. The vapours of thallium and sodium, especially thallium, extinguish the lines of coal-gas most easily, but one must raise the vapour of barium compounds to the highest possible temperature before it will make a coal-gas spectrum completely disappear.

Besides this, one finds in some of these bodies this property of extinguishing others. Thus the thallium flame extinguishes barium rays even to the point of masking the spectrum of a spark through barium. I shall return to this subject when describing my studies on the thallium spectrum.

Experience has taught me that, whilst conforming to the conditions mentioned above, I can use indifferently—as I have done—an oxyhydrogen or oxy-coal-gas blowpipe. In every case I checked my observations the one by the other.

Spectrum analysis of the electric arc passing between *pure* carbon electrodes, and charged with a compound of one of the metals mentioned above, led to results differing from those yielded by spectrum analysis of the oxy-coal-gas blowpipe charged with a compound of the same metals.

However intense the current producing the arc might be, the charging of it by the metallic compounds mentioned did not extinguish the electric carbon lines when they appeared. The spectrum seen showed at the same time, *with perfect clearness*, the characteristic carbon lines and bands, and the characteristic lines and bands of the metallic compound put into the *arc*. This spectrum showed the lines and bands of both spectra superposed.

When using carbon electrodes for forming the arc I had some work to do to pick out the lines belonging to the carbon spectrum and those belonging to the spectrum of the body put into the arc. I did this sorting with an arc charged with a compound of each of the metals.

In order to be able to make the selection, I first studied the spectrum of carbon in the arc, employing the spectroscope I had used to examine the *inner cone* of an oxy-coal-gas blowpipe flame brought to its *greatest* luminous intensity; I have given above the results of this latter examination.

When carrying on this delicate work I found, just as M. Fievez has done,* that the *number* and *position* of the lines and bands in an electric spectrum of carbon were identical with the *number* and *position* of the lines and bands in the flame spectrum of oxy-coal-gas.

I found this identity with an arc varying from 4 to 25 m.m. in length, both with the spectroscope I originally used and with different spectroscopes, as I shall mention later on.

When superposing a coal-gas spectrum on an electric spectrum of carbon, and showing, by this means, the identity of the number and position of the lines and bands in the two spectra, I found that the lines and bands in an electric spectrum of carbon *invariably* stood out on a *continuous* spectrum. *This continuous spectrum was entirely wanting in the appearance of a coal-gas spectrum*, whichever spectroscope might be used.

On account of the presence of a continuous spectrum, more or less intense, according to the luminous intensity of the arc passing between carbon electrodes, when putting into the arc a compound of which one wishes to form an electric spectrum, I have *always* placed the spectroscope at a suitable distance for diminishing, as far as possible, its intensity, whilst leaving to the lines and bands of the metallic compound sufficient luminosity to permit the identification of the electric carbon lines and bands, which retain sufficient luminosity, varying with the distance, to allow of a perfectly accurate identification.

One knows, besides, that when using a strong *though short* spark, or an electric discharge in air or hydrogen charged with a metallic compound, it is equally necessary to sort out in the spectrum seen the lines due to the metallic compound, the atmospheric lines and bands, and the hydrogen lines, which are produced at the same time. In my opinion the identification of the carbon bands and lines in the spectrum of an arc made by a current, though very trying to the eye, is easier, on account of the clearness of the lines, than that of the atmospheric bands and lines of the spark and electric discharge, which, however one makes it, always remain more or less diffused, very often masking the sharp definition of lines of the metallic compounds in their neighbourhood.

Notwithstanding all these difficulties, I used, *as a method of checking*, all these different means of producing an electric spectrum of the bodies on which I was carrying on my investigations.

(To be continued).

ON THE

ESTIMATION OF SIMPLE CYANIDES IN PRESENCE OF COMPOUND CYANIDES AND CERTAIN OTHER SUBSTANCES.

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Johannesburg, South Africa.

The presence of other cyanogen compounds may interfere very seriously with the correct estimation of the simple alkaline cyanide in a given solution. In the treatment of ores by cyanide, various compounds, such as ferrocyanides, sulphocyanides, &c., may be formed.

It is desirable to know the extent to which the presence of such bodies interfere with the estimation of the simple cyanide. A determination of the double cyanides themselves is also useful at times, since it may enable us to judge of the nature and extent of the decomposition of cyanide occurring during the leaching process, and to suggest a suitable means of diminishing this decomposition. It is also sometimes desirable to determine the quantity of the various cyanogen compounds in the solutions leaving the "precipitation-boxes," in order to ascertain the nature of the losses occurring in precipitation, and to decide what means may be adopted for recovering the cyanogen from the compound cyanides contained in these liquors.

I.

The following experiments were therefore made to determine the influence of various substances liable to occur in practice on the estimation of the simple cyanide.

A.—*Influence of Ferrocyanides.*

The presence of *ferrocyanides* interferes with the correct estimation of the cyanide by means of silver nitrate, causing the indications to be somewhat too high. The error is of importance, however, only when the percentage of cyanide is relatively small. The effect of varying quantities of ferrocyanide of potassium on the estimation of potassium cyanide is shown below. The standard ferrocyanide solution contained 0·5 per cent $K_4FeCy_6.3H_2O$.

No. of test.	Potassium cyanide, 0·1 per cent. C.c.	Potassium ferrocyanide, 0·5 per cent. C.c.	Standard $AgNO_3$ required. C.c.	Strength of KCy indicated. Per cent.	Percentage of error.
1.	25	—	2·5	0·1	—
2.	25	5	2·6	0·104	+4
3.	25	10	2·75	0·11	+10
4.	25	15	2·9	0·116	+16
5.	25	20	2·9	0·116	+16

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* "New Researches on the Carbon Spectrum," by Ch. Fievez (*Journal of the Royal Academy of Belgium*, 3rd Series, vol. xiv., p. 100).

The error introduced by the presence of ferrocyanide is less when the "iodine" method of titration is used, as shown by the following experiments:—

No. of test.	Potassium cyanide, 0·0954 per cent. C.c.	Potassium ferrocyanide, 0·5 per cent. C.c.	Standard iodine required. C.c.	Strength of KCy indicated. Per cent.	Percentage of error.
1.	25	—	7·45	0·0954	—
2.	25	5	7·50	0·0960	+0·63
3.	25	10	7·45	0·0954	—
4.	25	15	7·60	0·0973	+1·99
5.	25	20	7·55	0·0966	+1·27

B.—*Influence of Ferricyanides.*

The presence of *ferricyanides* interferes very slightly with the correct estimation of cyanide either by the silver nitrate or by the iodine method. When silver nitrate is used, a reddish brown precipitate of ferricyanide of silver at first appears instead of the white precipitate of cyanide of silver, and re-dissolves as long as an excess of cyanide is present.

A decinormal solution of ferricyanide of potassium was prepared, containing 32·9 grms. per litre.

A mixture was made of 10 c.c. 0·905 per cent potassium cyanide and 10 c.c. N/10 potassium ferricyanide.

This required 9 c.c. standard silver nitrate, indicating 0·9 per cent KCy.

The following tests were made by the iodine method:—

No. of test.	Potassium cyanide, 0·0947 per cent. C.c.	Potassium ferricyanide, 3·29 per cent. C.c.	Standard iodine required. C.c.	Strength of KCy indicated. Per cent.	Percentage of error.
1.	25	—	7·40	0·0947	—
2.	25	5	7·35	0·0941	−0·63
3.	25	10	7·35	0·0941	−0·63
4.	25	15	7·30	0·0934	−1·37
5.	25	20	7·25	0·0928	−2

The amount of cyanide may be estimated with tolerable accuracy by the iodine method in presence of both ferro- and ferricyanide in the same solution.

A mixture was made of 25 c.c. 0·5 per cent ferrocyanide, 10 c.c. 3·29 per cent ferricyanide, and 25 c.c. 0·098 per cent cyanide.

This required 7·3 c.c. standard iodine, indicating 0·1 per cent potassium cyanide, the end-point being quite sharp. The same mixture, tested by silver nitrate, required 3·1 c.c. indicating 0·124 per cent KCy, the end-point being rather indefinite.

C.—*Influence of Sulphocyanides.*

Sulphocyanide (thiocyanate) of ammonium interferes with the estimation by silver nitrate, rendering the end-point somewhat obscure. It does not appear to interfere with the iodine method.

An approximately decinormal solution of ammonium sulphocyanide was prepared.

(*a*) 25 c.c. 0·092 per cent KCy and 10 c.c. standard sulphocyanide required 23 c.c. $AgNO_3$, indicating 0·092 per cent KCy.

(*b*) 25 c.c. 0·092 per cent KCy and 25 c.c. standard sulphocyanide required 2·05 c.c. $AgNO_3$, indicating 0·082 per cent KCy.

(*c*) 10 c.c. 0·092 per cent KCy and 10 c.c. standard sulphocyanide required 2·75 c.c. standard iodine, indicating 0·092 per cent KCy. (1 c.c. iodine = 0·00334 grs. KCy).

D.—*Influence of Ammonium Carbonate.*

It has been pointed out by J. S. McArthur that the indications by the silver method are too high in presence of ammonium carbonate, and that the error may be rectified by the addition of potassium iodide, which forms iodide of silver, insoluble in ammonium salts. This statement was verified by the following experiments:—

No. of test.	KCy (0·094 per cent). C.c.	Decinormal $(NH_4)_2CO_3.H_2O$. C.c.	Standard $AgNO_3$ required. C.c.	Percentage of KCy indicated.	Remarks.
1.	25	—	2·35	0·094	Without KI.
2.	25	10	2·45	0·098	" "
3.	25	20	2·55	0·102	" "
4.	25	30	2·60	0·104	" "
5.	25	50	2·65	0·106	" "
6.	25	50	2·40	0·096	With KI.

E.—*Influence of Zinc Double Cyanide.*

In the presence of the alkaline double cyanides of zinc the indications by both methods are quite indefinite. When any appreciable quantity of zinc is present it is practically impossible to obtain a correct reading. When no other impurity is present the amount of simple cyanide may be arrived at from an estimation—

1. Of the "total cyanide," *i.e.*, the equivalent in potassium cyanide of all the cyanogen present;
2. Of the zinc, from which the amount of double cyanide (*e.g.*, K_2ZnCy_4) may be calculated.

II.

We have now to consider the estimation of the various compound cyanides, in presence of one another, and of the simple cyanides. For practical purposes no method is admissible which is not easily and rapidly executed, and which does not give perfectly definite and unmistakeable indications. Many of the methods commonly described in the text-books are therefore excluded.

A.—*Estimation of Ferrocyanides.*

In the absence of other reducing agents, the estimation of ferrocyanides may be carried out by the method of De Haen, which consists in diluting a measured volume of the solution, acidifying with sulphuric acid, and titrating with potassium permanganate. The presence of *cyanides* and *ferricyanides* does not interfere seriously with this reaction, but it is doubtful whether it would yield reliable results with the impure solutions from the leaching vats and "zinc-boxes." Probably Erlenmeyer's modification, in which the ferrocyanide is first precipitated as Prussian blue, would yield better results, but the estimation would be too tedious for general use.

A standard permanganate solution was prepared, such that—

1 c.c. = 0·04 grm. ferrocyanide ($K_4FeCy_6.3H_2O$).

The following tests were made:—

	(*a*).	(*b*).	(*c*).
0·5 per cent ferrocyanide taken	25 c.c.	50 c.c.	25 c.c.
N/10 ferricyanide taken	—	10 "	10 "
0·9 per cent cyanide taken ..	25 "	—	—
0·095 per cent cyanide taken ..	—	—	10 "
Permanganate required	3·1 "	6·2 "	3·05 "
Ferrocyanide indicated	0·496%	0·496%	0·488%

B.—*Estimation of Ferricyanides.*

The estimation of ferricyanides may be made by Lenssen's method, with Mohr's modification.

The presence of *ferrocyanides* does not interfere seriously. In the presence of *cyanides* the indications were found to be somewhat too low.

A decinormal solution of potassium ferricyanide was prepared. (32·9 grms. per litre).

The following tests were made (see Table next column).

C.—*Estimation of Zinc Double Cyanides.*

An approximate idea of the quantity of zinc in the solution may be obtained by adding a known excess of standard ferrocyanide, and titrating the acidulated solution with permanganate, as in De Haen's method. On

	(a).	(b).	(c).	(d).
N/10 ferricyanide taken, c.c.	10	10	10	10
0·5 per cent ferrocyanide added, ... c.c.	—	10	—	25
0·9 per cent cyanide added .. .. .. c.c.	—	—	10	—
0·095 per cent cyanide added .. .. .. c.c.	—	—	—	25
Potassium iodide added, grm.	1	1	1	1
Conc. hydrochloric acid added .. .. .. c.c.	2	2	2	2
Zinc sulphate (0·1 per cent Zn) added (neutralised with Na_2CO_3) .. c.c.	10	20	20	20
Number of determinations made	3	2	6	1
Mean N/10 thiosulphate required .. .. .. c.c.	10·03	9·68	9·67	10·05
Ferricyanide indicated, p.c.	3·28	3·27	3·17	3·3

addition of ferrocyanide to the zinc cyanide solution no precipitate is formed at first, but on acidulating the zinc is thrown down as an insoluble ferrocyanide which is unaffected by potassium permanganate. The difference between the amount of ferrocyanide added and the amount found therefore indicates the equivalent of the zinc present. The percentage of zinc found, multiplied by 4, indicates the percentage of potassium cyanide (KCy) which has entered into combination with zinc to form the double cyanide (K_2ZnCy_4).

The following tests were made :—

	(a).	(b).	(c).	(d).
0·9 per cent cyanide taken, c.c.	25	25	25	25
Zinc sulphate solution added .. .. .. c.c.	1	2	3	4
Containing zinc .. grm.	0·01	0·02	0·03	0·04
0·5 per cent ferrocyanide solution added .. c.c.	25	25	50	50
Containing ferrocyanide, grms.	0·125	0·125	0·25	0·25
Permanganate required, c.c.	2·1	1	2·85	1·75
Equivalent to ferrocyanide ..	0·084	0·04	0·114	0·07
Ferrocyanide combined with zinc	0·041	0·085	0·136	0·180
Ferrocyanide per grm. of zinc	4·1	4·25	4·5	4·5

Mean 4·34 grms.

Taking the atomic weight of zinc as 65, and the molecular weight of potassium ferrocyanide ($K_4FeCy_6.3H_2O$) as 422, then—

$$3Zn : 2(K_4FeCy_6.3H_2O) :: 1 : 4·33.$$

The mean of the four tests quoted above showed a proportion of 1 : 4·34.

It therefore appears probable that the following reaction takes place :—

$$3K_2ZnCy_4 + 2K_4FeCy_6 + 12H_2SO_4 = \\ = K_2Zn_3(FeCy_6)_2 + 12KHSO_4 + 12HCy.$$

D.—*Determination of "Total Cyanide" in presence of Zinc.*

If an excess of potassium ferrocyanide be added to a solution containing the zinc double cyanide, and the resulting solution be titrated with standard iodine, a few drops of dilute starch solution being used as indicator, we may determine the equivalent in potassium cyanide of the free alkaline cyanides and the zinc double cyanide. The cyanogen present as ferro- and ferricyanide is, of course, not determined. This method of estimating the "total cyanide" is much simpler and more rapid than the method by precipitation with sodium sulphide previously described (see CHEMICAL NEWS, vol. lxxi., 274), and appears to be equally accurate, provided that other substances capable of reacting with iodine are absent. Unfortunately, the solutions which pass through the zinc-boxes are subjected to the powerfully reducing action of nascent hydrogen, so that any indications obtained from them by the iodine method are of questionable value. The presence of alkaline sulphides, sulphites, or thiosulphates would be fatal to the estimation of cyanide by this method.

Solutions containing free hydrocyanic acid must first be neutralised by the addition of caustic soda. Solutions containing free caustic or monocarbonated alkali must first be neutralised by the addition of the necessary quantity of hydrochloric acid (see CHEMICAL NEWS, vol. lxxi., pp. 93, 274).

The following equation affords a simple explanation of the observed result, though several others are possible :—

$$2K_2ZnCy_4 + K_4FeCy_6 + 8I_2 = Zn_2(FeCy_6) + 8KI + 8ICy.$$

In any case the cyanogen of the zinc double cyanide is determined as though it existed as free KCy. The zinc ferrocyanide comes down as a dense white precipitate before the end of the reaction, which, however, does not interfere with the observation of the end-point.

With the limitation pointed out above this method yields excellent results.

(*a*) A mixture was made of 10 c.c. 0·093 per cent KCy and 1 c.c. pure $ZnSO_4$ (containing 0·001 grm. Zn).

This required from 2·3 to 2·55 c.c. of standard iodine, indicating 0·074 to 0·082 per cent KCy, the end-point being quite indefinite.

The same mixture, to which 5 c.c. of 0·5 per cent ferrocyanide were added, required 2·9 c.c. of standard iodine, the end-reaction being perfectly sharp, indicating 0·093 per cent KCy.

(*b*) A mixture was made of 10 c.c. 0·25 per cent KCy and 0·5 c.c. pure $ZnSO_4$ (containing 0·005 grm. Zn).

By direct titration with iodine the indications were quite indefinite, from 0·11 to 0·15 per cent. After adding 10 c.c. of 0·5 per cent ferrocyanide and titrating, 7·65 c.c. iodine were required, indicating 0·245 per cent KCy.

(*c*) A mixture was made of 40 c.c. 0·25 per cent KCy and 10 c.c. pure $ZnSO_4$ (containing 0·01 grm. Zn).

10 c.c. of this liquid should therefore contain 0·02 grm. KCy and 0·002 grm. Zn.

The mixture was shaken up with lime and filtered. 10 c.c. of the filtrate were mixed with 1·5 c.c. standard silver nitrate, which gave a strong turbidity, and titrated with N/10 hydrochloric acid, using phenolphthalein as indicator. 1·9 c.c. of acid were required. Another 10 c.c. of the filtrate were mixed with 1·9 c.c. N/10 hydrochloric acid, and 10 c.c. of 0·5 per cent ferrocyanide. This was titrated with standard iodine, 6·15 c.c. of which were required, indicating 0·0197 grm. KCy (by theory, 0·02).

(*d*) A solution from the "zinc-boxes" was tested as follows :—10 c.c. of solution and 10 c.c. of 0·5 per cent ferrocyanide required 2·5 c.c. standard iodine. 25 c.c. of solution and 10 c.c. of 0·5 per cent ferrocyanide required 6·25 c.c. standard iodine.

Both tests indicating 0·0825 per cent KCy.

Johannesburg, July 5, 1895.

Study of certain Varieties of Graphite.—Henri Moissan.—The author has compared the graphite described in the foregoing paper with the graphite of Ceylon, Borrowdale, Ticondoroga, Greenville, Omesnack (Greenland), Mugrau (Bohemia), Scharzbach, and South Australia. He concludes that the graphites occurring in nature may be classified, as proposed by Sn. Luzzi, as sprouting and non-sprouting varieties. The former seem to have been produced by the action of melted baths, especially metallic baths. The latter may be due to the action of a high temperature on any kind of amorphous carbon.—*Comptes Rendus*, cxxi., No. 17.

SPECIFIC VOLUME AND THE GENESIS OF THE ELEMENTS.

By C. T. BLANSHARD, M.A.

As I anticipated in a recent article in this journal (Chem. News. lxxi., p. 285), on "Melting-points of the Elements as a Clue to their Genesis," the question of Atomic and specific volumes provides a further clue. The atomic volumes of certain of the elements will be found to *alternate* in two different ways. It will also be found that the specific volumes, as calculated from observed specific gravities, in certain series of organic compounds, offer striking parallels to various conditions that maintain with the elements.

To take the first case of alternation of atomic volumes of the elements.

If the chemical elements are arranged in numbered series, we find in the eight series represented, that the atomic volumes (with the exceptions of the last three elements in series 2, 6, and 10, and the first two in series 3) alternately rise and fall; *i.e.*, in the odd-numbered series the atomic volumes regularly rise, whilst in the even-numbered series the atomic volumes regularly fall.

1. Hydrogen series.

2.	Li	Be	B	C	N	O	F
At. vol.	11·9	4·9	4·13	3·41	15·6	14·3	—
3.	Na	Mg	Al	Si	P	S	Cl
At. vol.	23·8	13·9	10·4	11·8	14·1	15·4	24·3
4.	K	Ca	Sc	Ti	V	Cr	Mn
At. vol.	44·9	25·6	—	—	9·3	7·45	7·45
		Fe	Co	Ni			
,, ,,		7·1	6·9	6·5			
5.	Cu	Zn	Ga	Ge	As	Se	Br
At. vol.	7·0	9·2	11·8	13·2	15·9	17·6	25·0
6.	Ru	Sr	Y	Zr	Nb	Mo	—
At. vol.	56·4	33·9	—	21·8?	13·3	11·2?	—
		Ru	Rh	Pd			
,, ,,		8·0	8·5	8·8			
7.	Ag	Cd	In	Sn	Sb	Te	I
At. vol.	10·2	13·1	15·3	16·2	17·9	19·5	25·6
8.	Cs	Ba	La	Ce	Nd	Pr	—
At. vol.	70·7	36·5	22·6	21·1	—	—	—
9.	Sa	—	Gd	Tb	—	Er	—
10.	Dp	Yb	—	—	Ta	W	—
At. vol.	—				17·6	9·8	
		Os	Ir	Pt			
,, ,,		8·5	9·0	9·1			
11.	Au	Hg	Tl	Pb	Bi	—	—
At. vol.	10·2	14·7	17·2	18·2	21·4	—	—
12.	—	—	—	Th	—	U	—
At vol.	—	—	—	21·1	—	12·8	—

Series 9 should prove to possess rising atomic volumes; that is to say, as the atomic weight increases there will be less and less corresponding increase in specific gravity. The figures for the atomic volumes are those calculated for a table given in Chem. News, vol. lxx., p. 271, except that more recent values of barium (Ba = 137·43) and cadmium (Cd = 112·06) are taken.

The second way of showing the alternation of atomic volume is by comparing the elements in their natural groups and noting the *differences* between the atomic volumes, as Bazaroff has done in the case of atomic weights. It will be seen that—

1. The differences between the atomic volumes of elements, taken in natural groups, alternate in groups I. and II., and probably also in III. and IV.
2. In V. and VI. the differences increase with the increase in atomic weight.
3. In group VII. the differences are constant.
4. In all the *a* and in all the *b* groups the differences become less with increase in atomic weight.

Group.	Element.	At. vol.	Diff.
I.	Li	11·9	
			11·9
	Na	23·8	
			21·1
	K	44·9	
			11·5
	Rb	56·4	
			14·3
	Cs	70·7	
II.	Be	4·9	
			9·0
	Mg	13·9	
			11·7
	Ca	25·6	
			8·3
	Sr	33·9	
			12·7
	Ba	36·6	
III. IV.	Data too defective.		
V.	N	15·6	
			−1·5
	P (red)	14·1	
			+1·8
	As (am.)	15·9	
			2·0
	Sb	17·9	
			3·5
	Bi	21·4	
VI.	O	14·3	
			1·15
	S (rhom).	15·45	
			2·12
	Se (cryst.)	17·57	
			2·42
	Te (cryst.)	19·99	
VII.	F	—	
			—
	Cl	24·3	
			0·7
	Br	25·0	
			0·6
	I	25·6	
I.*a*.	Cu	7·0	
			3·25
	Ag	10·25	
			−0·05
	Au	10·20	
II.*a*.	Zn	9·2	
			3·9
	Cd	13·1	
			1·6
	Hg	14·7	
III.*a*.	Ga	11·8	
			3·5
	In	15·3	
			1·9
	Tl	17·2	
IV.*a*.	Ge	13·2	
			3·0
	Sn	16·2	
			2·0
	Pb	18·2	

Group.	Element.	At. vol.	Diff.
V.*a*.	V	9·31	
			3·99
	Nb	13·3	
VI.*a*.	Cr	7·45	
			3·72
	Mo	11·17 ?	
			1·52
	U	12·79	
VII.*a*.	Mn	7·45	
II.*b*.	Fe	7·1	
			0·95
	Ru	8·05	
			0·45
	Os	8·50	
IV.*b*.	Co	6·89	
			1·61
	Rh	8·50	
			0·47
	Ir	8·97	
VI.*b*.	Ni	6·53	
			2·24
	Pd	8·77	
			0·29
	Pt	9·06	

The *c* groups do not supply any data, as, being Preyer's series 10 and 11, at most each *c* group contains two elements. But it may be noted, in confirmation of Prof. Preyer's classification, which places Tantalum in what I term group V.*c*, instead of with Vanadium and Niobium in V.*a*; that the atomic volume of Ta, 17·6, shows a difference of 4·3 from that of Nb; whereas, by the above laws of differences of atomic volumes, were Ta the third member of the group V.*a*, it would show a difference of considerably *less* than 3·99, namely, a difference of about 1·6. The *b* groups in the above classification are Mendeleeff's group, VIII.

The *a* groups may be aptly termed the *copper*, and *b* the *iron groups*. With regard to the differences in atomic volume, it may be further noted that—

5. In the ordinary groups the first differences are low, succeeded by higher ones.

6. In the copper and iron groups (or *a* and *b* groups) the first differences are high, succeeded by lower ones.

(To be continued).

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Continued from p. 214).

The fourth class of mixtures, of which the only representative here is the mixture of nitrobenzene and carbon tetrachloride, does not, in reality, belong to our subject of investigation, which is to study mixtures of volatile liquids only, and not those of a volatile with an almost involatile one. Still it was thought advisable to find out what the partial tensions of mixtures of such liquids would be, inasmuch as Raoult (*loc. cit.*) has made an elaborate study of the total vapour-tension of mixtures of ether and several almost non-volatile liquids. As is seen in the curve, the partial pressure of the carbon tetrachloride and the total pressure of the mixture are almost identical, just as would naturally be expected. The curves are, if we regard the right hand ordinate first, at the beginning parallel with the straight line connecting the points representing the vapour-tensions of the pure liquids; they then turn upwards, reach a maximum distance from the straight line at about the abscissæ value of fifty, and then gradually turn downwards towards the origin. I was curious to see if this behaviour was characteristic of the mixtures of liquids investigated by Raoult.

Accordingly I have re-calculated his data so as to get them into a form comparable with mine. These re-calculated data are given in the following small Tables:—

Table A.—*Vapour-Tensions of Solutions of Turpentine in Ether at 16·2°.*

Vapour-tension of Turpentine at 16·2° is 4 m.m. of Mercury.

Vapour-tension of Ether at 16·2° is 377 m.m. of Mercury.

Mols. of Turpentine in 100 mols. of solution.	Vapour-tension in m.m. of Mercury.
5·9	354
12·1	332
23·4	294
35·5	255
47·9	212
64·5	159

Table B.—*Vapour-Tension of Solutions of Nitrobenzene in Ether at 16·0°.*

Vapour-tension of Nitrobenzene at 16·0° is 4 m.m. of Mercury.

Vapour-tension of Ether at 16·0° is 374 m.m. of Mercury.

Mols. of Nitrobenzene in 100 mols. of solution.	Vapour-tension in m.m. of Mercury.
6·0	353
17·9	321
35·5	278
56·2	232
75·9	166
84·0	132

Table C.—*Vapour-Tensions of Solutions of Aniline in Ether at 15·3°.*

Vapour-tension of Aniline at 15·3° is 4 m.m. of Mercury.

Vapour-tension of Ether at 15·3° is 364 m.m. of Mercury.

Mols. of Aniline in 100 mols. of solution.	Vapour-tension in m.m. of Mercury.
3·8	349
7·7	335
14·8	308
20·5	292
49·6	210
68·7	147

Table D.—*Vapour-Tension of Solutions of Methyl Salicylate in Ether at 14·2°.*

Vapour-tension of Methyl Salicylate at 14·2° is 4 m.m. of Mercury.

Vapour-tension of Ether at 14·2° is 306 m.m. of Mercury.

Mols. of Methyl Salicylate in 100 mols. of solution.	Vapour-tension in m.m. of Mercury.
1·1	344·6
2·1	343·6
4·8	332·0
9·2	316·0
15·1	301·0
23·2	281
49·0	208
77·0	125
85·0	101

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* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

Table E.—*Vapour-Tensions of Solutions of Ethyl Benzoate in Ether at 11·7°.*

Vapour-tension of Ethyl Benzoate at 11·7° is 3 m.m. of Mercury.

Vapour-tension of Ether at 11·7° is 313 m.m. of Mercury.

Mols. of Ethyl Benzoate in 100 mols. of solution.	Vapour-tension in m.m. of Mercury.
4·9	296
9·6	286
27·1	235
53·0	167
75·5	94
94·4	39

If these results be plotted in a system of co-ordinates, the curves will be found to have a close resemblance to the one which I have found for the mixture of nitrobenzene and carbon tetrachloride. It seems likely that this form of curve is the general one for the total tension of mixtures of a volatile with an almost fixed liquid.

(To be continued).

NOTICES OF BOOKS.

The Scientific Foundations of Analytical Chemistry treated in an Elementary Manner. By Wilhelm Ostwald, Ph.D., Professor of Chemistry in the University of Leipzig. Translated, with the Author's sanction, by George McGowan, Ph.D. 8vo., pp. 208. London and New York: Macmillan and Co. 1895.

Professor Ostwald's work here before us is clearly distinct from the other analytical manuals, large or small, with which we have come in contact. It is concerned not with technical details, but with fundamental principles. Hence, whilst it would not be consulted with reference to the best method of analysing a complex phosphate or titaniferous iron, or a cobalt ore, it may, and should be, considered not merely by the student, but by the experienced practitioner.

We are here reminded that no substance is absolutely insoluble, and that none of our methods of separation and determination are perfect. Suggestions are thrown out which deserve notice. Thus, when speaking of the separation of solids from each other, the author mentions that mixtures of different substances in powder are electrified on shaking, one constituent becoming positive and the other negative. If the mixture is thrown upon an electrified non-conductor, the oppositely charged particles are attracted to it and the others repelled. Again, in a non-homogeneous electrical field the substances with the higher dielectric constants are driven to those spots where the intensity of the field is greatest. No analytical application of this fact has yet been made.

In speaking of the treatment of precipitates, attention is called to the phenomena of *ad*sorption—not to be confounded with *ab*sorption.

In the separation of gases from each other we are reminded that not all possible methods have been tried in analysis.

The theory of removing a dissolved substance from the solvent by shaking it up with another is clearly expounded. It is shown that with a given quantity of solvent a more perfect separation is effected if the shaking up is done with many small successive portions rather than with a few large ones.

Concerning heterogeneous equilibrium, the law is laid down that—"In two contiguous spaces or phases the concentration of each substance present in both spaces must bear a constant ratio."

It is admitted that the attempts made to determine the amount of a precipitate without washing it, from the mean specific gravity of precipitate *plus* liquid and the specific gravity of liquid alone, have led to no satisfactory results.

The second part of the book shows the application of the principles already laid down. Professor Ostwald repeats that "students who read this book will do so, not so much with the object of learning analytical chemistry from it, as of pondering over the scientific principles which underlie what they have already been taught by actual practice, so as to be able to apply this knowledge with greater freedom and certainty."

We can only hope that many students will thus ponder over these principles.

We regret to find that Dr. McGowan uses as an abridgment for "cubic centimetre," not the simple and unmistakeable c.c., as used in France and hitherto in Britain, but the more prolix German expression c.cm.

Report of the Trinidad Government Analyst. Minute (No. 63) from the Acting Governor, accompanying the Annual Report of the Government Analyst for 1894. Trinidad: Government Printing Office, Port-of-Spain.

The total number of samples examined during the year was 653, of which 626 were official samples. The official samples were sent in by the police in connection with cases before the Courts of Justice, from the sanitary police (food and drugs), the Customs, the Board of Health, the receiver-general, the surgeon-general, and Public Works. Of the official samples 78 were connected with charges of murder, wounding, and indecent assaults; and 69 were cases of suspected poisoning. In 38 of these samples poisons were detected, namely arsenic, mercuric chloride, potassium cyanide, creosote, and preparations of opium. None of the insufficiently known poisonous products of tropical countries seem to have been used.

The adulteration of milk still requires constant vigilance, as 36 per cent of the total samples had been let down with water in the proportion of 25 per cent. Oleomargarine is sold at the same price as butter.

We regret to find that the Colony is adopting the recent error of the home-kingdoms in requiring an addition of mineral oils to methylated spirits. Why not, as is done in Germany, make the methylated spirit undrinkable by the addition of a trace of Dippel's animal oil?

The question of a regular bacteriological examination of water supplied to Port-of-Spain is still under consideration.

Some samples of water from wells in Tacarigua district were found to be worse than many sewage effluents.

Agricultural Journal. Published by the Department of Agriculture of the Cape Colony. Vol. viii., No. 17.

Attention is emphatically called to the value of the sunflower to farmers. It is found to bear the intense heat of central Australia better than any other crop. The seed is an excellent food for poultry. An acre of land yields 50 bushels of seed, from which 50 gallons of oil may be obtained. The oil is excellent for lubricating, and for the manufacture of superior toilet soap, as well as for a clean-burning lamp-oil. The cake left after the expression of the oil is a good cattle-food, being considered in Eastern Europe as the best available cattle-food, superior to rape or hemp cake: 1000 lbs. of dried stalks have been found to yield 57 lbs. of ash, chiefly potash. Hence the stalks and leaves should always be ploughed into the soil.

Particular attention is called to the war against the scale-insects (*Coccidæ*), which have already destroyed the orange and lemon plantations of South Africa. For dealing with these pests an emulsion of paraffin is recommended. A favourite formula is—

Paraffin..	2 gallons.
Soap	½ lb.
Water	1 gallon.

The water is heated to boiling, the soap stirred in until dissolved; when the mixture is just below a boiling heat the paraffin is stirred in with violent agitation for ten minutes.

Determination of the Atomic Weight of Cobalt. An Inaugural Dissertation presented to the Philosophical Faculty of the University of Basle for obtaining the Degree of Ph.D. By Hermann Thiele. Submitted December 15th, 1894. Basle: Kreis Printing Works. 1895.

The author, in criticising the researches of Remmler (*Zeitsch. f. Anorg. Chemie*, ii., p. 221), points it out as a singular fact that the atomic weight of the several fractions operated on by the latter does not rise or fall progressively, but fluctuates up and down. Remmler explains this fact by the presence in the fractions of different quantities of an unknown element, as admitted by Krüss. Hence the investigation had even a greater importance than might have been supposed at first sight, though Dr. Thiele did not find it useful to fractionate the specimens employed in most of his experiments.

He used three methods:—1, weighing cobaltous oxide and the metal; 2, cobaltous chloride and the metal; and 3, weighing the metal and silver chloride. The three determinations made by the first method give an average atomic weight = 58·849. By the second method, six determinations show an average = 58·64; and by the third method, four determinations gave a mean value of 58·801, or, with a correction for the solubility of AgCl in water, 58·770. All the results are calculated for

$$O = 15{\cdot}96,\ Cl = 35{\cdot}37,\ \text{and}\ Ag = 107{\cdot}66.$$

The author's researches point to a probable value:—Co = 58·765. This result is compared with the most trustworthy recent determinations, *i.e.*, those of Russell 58·59, Lee 58·97, Zimmermann 58·74, and Winkler 59·67. Hence it is pointed out that the author's result agrees exceedingly well with that of Zimmermann, whilst the values of Russell and Lee diverge equally far on each side. Dr. Thiele's results cannot be at all reconciled with that of Winkler. It is stated in a final note that this dissertation was handed in to the Philosophical Faculty of Basle on December 15th, 1894. Hence no reference could be made in it to the subsequent investigations of Winkler (*Zeitsch. f. Anorg. Chemie*, viii., p. 291).

Incidentally it is remarked that we can depend but little upon weights, originally extremely accurate, if they have been used for some time, however carefully.

A careful examination of this pamphlet will convince the reader that Dr. Thiele has used every precaution. His weights (made by Verbeck, of Dresden) displayed, as far as those below 10 grms. are concerned, only in two cases an error of 0·02 m.grm. The weights above 10 grms. were used only for counterpoises, so that their absolute accuracy does not come in question. The balance was made by Bekel, of Hamburg, and had been carefully tested as regards the constancy of its zero-point. The vessels employed were of platinum, or, where this material was impracticable, of Meissen porcelain, or of the so-called "resistance glass" of Koehler and Martini.

Transactions of the Wagner Free Institute of Science of Philadelphia. Vol. iii., Part 3, March, 1895. Philadelphia: Wagner Free Institute of Science.

The issue before us is entirely devoted to geology and palæontology, and consequently contains no matter which rightfully falls within our purview.

The Free Institute has a faculty comprising departments of chemistry, botany and forestry, geology, physics and astronomy, literature and history, and engineering. Biology seems to have been overlooked. If we might so far presume we would suggest that a biological department should be established, and literatnre and history eliminated. We throw out this hint because we observe that in the so-called "literary and philosophical societies" of England, literature monopolises the lion's share of attention, and finds a space in the *Transactions*.

Practical Proofs of Chemical Laws. A Course of Experiments upon the Combining Proportions of the Chemical Elements. By Vaughan Cornish, M.Sc., Associate of the Owens College, Manchester. London and New York: Longmans, Green, and Co. 1895. Pp. 92.

If the multitude of works destined to throw a guiding light upon the course of the chemical student has any prophetical meaning, we ought soon to have a most luxuriant harvest of discoverers and discoveries. Mr. Cornish admits, in his Preface, that the "experimental proofs" might more properly be called "verifications." Without doubt they constitute a useful series of exercises for students who are already acquainted with the qualitative composition of the substances employed, and as such the book deserves recommendation.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 17, October 21, 1895.

The Secretary announced the death of Dr. Hellriegel, a correspondent of the Section of Rural Economy, who died on September 24th last at Bernburg (Anhalt). M. Berthelot added that the deceased is distinguished for his beautiful researches on the fixation of nitrogen by leguminous plants, a phenomenon which he successfully traced to the action of bacteria inhabiting certain nodosities on the roots of the vegetables.

Study of a Graphite Extracted from a Pegmatite.—Henri Moissan.—This paper will be inserted in full.

Study of the Latent Heats of Evaporation of the Acetones of the Fatty Series, Octane, Decane, and of the Two Ethers of Carbonic Acid.—W. Louguinine.—From his experiments the author concludes that for each of the groups which have been studied the volume of $\frac{M\,S}{T}$ is approximately constant. In this expression M represents the molecular weight of the substance, S its latent heat of evaporation, and T its absolute temperature of ebullition. For different groups of substances it varies in a decided manner (from 26·5 to 19·8).

Potassic Peroxidic Derivatives of Benzoquinone.—Ch. Astre.—The author's results show the diketonic nature of benzoquinone.

Composition of the Rices Imported into France.—M. Balland.—Rice is a more nutritive aliment than is commonly supposed, and it would be advantageous to restrict the use of glazed rices, and to favour the consumption of the natural grain simply deprived of its husk.

Toxicity of Acetylene.—M. Gréhant.—The author infers from his experiments that acetylene is poisonous if inhaled in large quantities. This gas can be easily detected in the blood by means of the "grisometer." It is, however, much less poisonous than coal-gas. Its mixtures with oxygen are highly explosive.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 14, 1895.

Action of Nitrogen Peroxide upon the Haloid Salts of Antimony.—V. Thomas.—On dissolving a haloid antimony salt either in chloroform or in carbon disulphide, and passing into the solution a current of nitric oxide, we generally obtain a white crystalline precipitate, which, however, ceases to form after a certain time. The author thought that it might be due to traces of nitrous vapour. He took a stoppered flask, from which the air had been carefully expelled by a current of carbonic acid, and containing a chloroformic solution of antimony trichloride. Into this was passed a current of dry nitrous oxide, perfectly free from peroxide. No precipitate was formed until the flask was unstoppered, when it was immediately formed. The precipitate had the composition $Sb_4O_{11}N_2Cl_4$. With tribromide dissolved in chloroform the result is analogous, but the precipitate contains no bromine, and has the composition $Sb_4O_{15}N$.

Molecular Modifications of Glucose.—C. Tanret.—The author calls the ordinary glucose α, that which when crystallised gives the highest rotatory-power $\alpha_D = +106°$; glucose β is the modification of a constant rotatory-power $\alpha_D = +52{\cdot}5°$; and glucose γ is that which gives at once the lowest rotatory-power $\alpha_D = +22{\cdot}50°$.

New Synthesis of Some Aromatic Nitriles.—A. Desprez.—The author has supposed that cyanogen, like chlorine, might be substituted for hydrogen in organic compounds. He applied the process for the present to five carbides, which he succeeded in transforming into nitriles, namely, benzene, toluene, two xylenes, and mesitylene.

Causes of the Colouration and Coagulation of Milk by Heat. Formation of Formic Acid at the Expense of Lactose.—P. Cazeneuve and E. Haddon.—Already noticed.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 116.

Combustion of Mineral Oils in Common Lamps.—P. Kouindjy.—This paper cannot be reproduced without the four accompanying figures.

Matches with Explosive Pastes.—Th. Schlœsing.—The entire replacement of phosphorus in the manufacture of matches does not seem to be as yet very near. Even the substitution of explosive pastes for those with white phosphorus is not so simple a matter as it might seem at first sight.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on November 4th, Sir James Crichton-Browne presiding. The following were elected Members:—H.R.H. Prince Louis Philippe, Duc d'Orleans, Sir John Evans, K.C.B., F.R.S., The Hon. Adrian Verney Verney Cave, Mr. Walter Allcroft, and Mr. James Beale. The Managers reported that the late Mr. John Bell Sedgwick, M.R.I., had bequeathed £300 to the Royal Institution in aid of the Fund for the Promotion of Experimental Research at Low Temperatures. The special thanks of the Members were returned to Sir Frederick Abel, Bart., for his donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures.

Conversazione at the Melbourne College of Pharmacy.—This very successful demonstration comprehended an exhibition of specimens and appliances bearing on pharmacy, such as plants of medicinal and technical interest, polariscopes and micro-spectroscopes (both instruments which ought to be more familiar to the pharmacist than they generally are), collections of useful and destructive insects, bacteriological specimens, fluorescent liquids, &c. As an instance of utter irrelevance there figured a "philatelic" collection. A short lecture was given by Dr. F. Howell Cole on "Toxins and Antitoxins," and one by Mr. Plowman on "The Romance of Cocaine." A prolonged investigation on a case of arsenical poisoning did not involve any analytical question. In a prosecution at Adelaide, under the Food and Drugs Act, the question was raised "What is vinegar?" The City Analyst held that vinegar for dietetic use should be composed of alcohol, mucilage, extractive matter, acetic acid, and acetic ether. The University Analyst maintained that the term vinegar was a generic one, and should mean a naturally fermented vegetable infusion. Mr. Scammell declared that pure acetic acid and water was vinegar, and that fermentation was not necessary. — *The Pharmaceutical Journal of Australasia.*

THE CHEMICAL NEWS.

Vol. LXXII., No. 1877.

NOTE ON THE
FORMATION OF CITRIC ACID BY THE OXIDATION OF CANE-SUGAR.

By ALFRED B. SEARLE and ARNOLD R. TANKARD.

Since the publication of Dr. Phipson's third note on the formation of citric acid by the oxidation of cane-sugar, we have continued our experiments on this subject, and have attempted to obtain citric acid by a strict adherence to the conditions last prescribed by Dr. Phipson (Chem. News, vol. lxxii., p. 190).

Equal weights of cane-sugar, concentrated nitric acid (sp. gr. 1·42), and potassium permanganate were taken, the last-named reagent being added in the form of a strong aqueous solution. The liquid became as clear as water in about half an hour after the last addition of permanganate. This solution was then allowed to stand for twenty-four hours, and at the end of that time was neutralised by the cautious addition of chalk, the liquid being frequently agitated. When the liquid ceased to have an acid reaction to litmus, it was filtered and the filtrate boiled for some minutes. No precipitate was produced even after the addition of a strong solution of calcium chloride and further boiling, thus showing the absence of any notable quantity of citrate.

The matter on the filter dissolved *with effervescence* in acetic acid, showing that an excess of calcium carbonate had been used. We fail to see how Dr. Phipson avoided the use of an excess of calcium carbonate in neutralising the acid solution.

We have also used sulphuric acid in place of nitric acid for acidulating the cane-sugar solution. In this case, the clear solution, after standing in the cold for twenty-four hours, was neutralised by the addition of chalk, and filtered. This filtrate, on boiling for some time, deposited a white crystalline precipitate, which was filtered off and washed with hot water. It was then dried at 100° C., and subjected to such tests as were described in our previous paper (Chemical News, vol. lxxii., p. 31).

The results in every respect confirmed those formerly obtained, and showed the substance to be composed entirely of hydrated calcium sulphate, $CaSO_4.2H_2O$.

Dr. Phipson, in his third note (Chemical News, vol. lxxii., p. 190), states that it is easy to point out where our error lies, but that it will perhaps not be so easy to get us to acknowledge it. We do not deny that citric acid may be formed by the oxidation of cane-sugar under suitable conditions, but we do assert that the mode of operating prescribed by Dr. Phipson fails to produce citric acid.

We notice that Dr. Phipson's first note on this subject (Chemical News, vol. lxxi., p. 296) was entitled "The Production of Citric Acid by the Oxidation of Cane-sugar." His second note was headed "On the Production of Citric Acid from Cane-sugar." His third note, however, has the heading "Citric and Tartaric Acids from Cane-sugar," and, indeed, this note seems to be mostly concerned with the formation of tartaric acid, whilst citric acid receives very bare mention. We do not dispute the fact that tartaric acid is a product of the oxidation of cane-sugar. Many observers have confirmed this; in fact, in his second note, Dr. Phipson gives references. But Dr. Phipson appears to be diverging from the question originally at issue, namely, Can citric acid be produced by the oxidation of cane-sugar *under the above conditions?*

Dr. Phipson states (Chemical News, vol. lxxii., p. 100) that we first failed because we used too much sulphuric acid; then, because we did not separate the organic acid by alcohol; and thirdly, because we used an insufficient quantity of permanganate (Chemical News, vol. lxxii., p. 190). The first and last of these objections, which have reference to the relative amounts of reagents employed, are now removed by the description of the process given by Dr. Phipson in his third note, but *still* we obtain no citric acid!

Regarding the use of alcohol for the separation of the organic acid, if it is so necessary for the success of the experiment as Dr. Phipson implies in his second note, it is strange that all mention of alcohol is omitted from his third note.

From the results of our experiments we are bound to conclude that citric acid cannot be obtained by the oxidation of cane-sugar in the manner prescribed by Dr. Phipson, and we observe that Mr. E. F. Hicks (Chem. News, vol. lxxii., p. 165) has independently arrived at the same conclusion.

67, Surrey Street, Sheffield,
November 4, 1895.

STUDY OF THE GRAPHITE EXTRACTED FROM PEGMATITE.

By HENRI MOISSAN.

We have established in previous researches that a sufficient rise of temperature at the ordinary pressure converts every variety of carbon into graphite. We have further shown that all the graphites produced in a bath of melted metal (iron, chrome, tungsten, molybdenum, vanadium, platinum, &c.) sprout. On the contrary, the graphites obtained by the volatilisation of carbon in the electric arc or by a simple thermic transformation do not present the property of sprouting when heated after the addition of a trace of nitric acid. These researches have led us to resume the study of some natural graphites.

It is known that Berthelot has given the following definition of graphite:—"Every variety of carbon capable of yielding a graphitic oxide on oxidation."

This graphitic oxide is most commonly obtained by Brodie's method on submitting graphite to the action of a mixture of potassium chlorate and nitric acid. We observe that on projecting very dry potassium chlorate into very concentrated nitric acid it dissolves instantly with an orange-red colouration, and under these conditions, whatever variety of graphite is used, we obtain at the temperature of 60°, after an action of ten hours, an entire transformation into graphitic oxide. The slightest trace of moisture prevents this red colouration, and greatly diminishes the speed of the transformation.

The specimen of graphite which I have studied was obtained from a pegmatite from America without specification of the locality.

This pegmatite is highly interesting, since we know that this eruptive rock has reached the surface after having reached a high temperature.

In this specimen the graphite appears in fine laminar crystals, the sides of which often measure more than a centimetre, and are intimately distributed throughout the entire mass. It is easy to separate the graphite by treating the rock in its native state repeatedly in the water-bath with hydrofluoric acid at a concentration of 50 per cent. All the felspar and silica quickly disappear. The residual matter is washed with boiling water and dried in the stove.

The pegmatite studied contained 12·77 per cent of graphite. The fine laminæ thus obtained are flexible, specular, and present a surface showing striæ and equilateral triangular impressions, perfectly characteristic.

This graphite takes fire in oxygen at the temperature of 690°; it yielded 5·01 per cent of ashes, composed chiefly of silica, alumina, and lime, and traces of iron.

This last metal has been detected by means of potassium sulphocyanide and ferrocyanide. The ash is white, and retains the form of the crystals of graphite. Its temperature of combustion is higher than that of the graphites of Scharzbach or of Ceylon.

This graphite sprouts. If it is moistened with monohydrated nitric acid, as Sn. Luzzi recommends, and then heated to dull redness, it sprouts abundantly.

If this graphite is treated with the oxidising mixture of potassium chlorate and of monohydrated nitric acid in large excess, there is presented a very curious phenomenon. We placed 6 grms. of graphite in a flask holding 500 c.c. along with a pinch of potassium chlorate and about 20 c.c. of nitric acid. At the outset of the reaction the graphite takes a fine greenish tint, due to a superficial reaction, and after some hours it increases in bulk in the liquid so as to fill half the flask. On a second attack it continues to sprout, and its bulk increases so that the vessel must be changed. This is the only graphite which in a liquid like nitric acid gives such an increase of volume at the temperature of 60°. After the deflagration of the graphitic oxide and its destruction, we did not find in the residue any trace of diamond, either black or transparent.

On the seventh attack with the oxidising mixture, the transformation into light green graphitic oxide is complete, but on a succeeding attack the graphitic oxide is absolutely decolourised.

On examining with a low microscopic power the fragments of quartz or of felspar to which the crystals of graphite were attached, I was much surprised to see that they presented impressions the exact image of the surface of these crystals. There are the same striæ and the same triangles, which a very energetic friction cannot remove.

This fact leads us to think that the graphite existed prior to the rocks which produced pegmatite by their crystallisation. This graphite, by its characteristic properties, completely recalls the specimens obtained in metals in a state of fusion in an electric furnace. It must have been produced under the same conditions, and at the moment of formation of pegmatite it has been moulded by the crystals of quartz and of felspar, and has left upon the latter the impression found upon its surface. —*Comptes Rendus*, cxxi., p. 538.

A NEW SPECTRAL PHOTOMETER.

By A. KŒNIG.

Between the collimator-tube, which has the superjacent slits always of equal width, and the eye-tube there is introduced a flint-glass prism, and further towards the eye-piece a twin-prism; that is, a combination of two flat prisms, touching each other with their thick ends (such, *e.g.*, as are used in Fresnel's interference experiment), and towards the collimator a so-called Rochon's prism. By means of this arrangement there are produced eight spectra, in one plane of which three times two each coincide with each other, and of which each pair are polarised vertically to one another. In the plane in which the spectra appear there is a diaphragm which, at the spot where two spectra polarised vertically to each other coincide, possesses a slit, through which therefore a given colour is cut out of both prisms. If we look through the slit towards the twin prism its entire surface is illuminated with spectral light, and we see the upper half of the field of vision illuminated with light of the one spectrum, and the lower half with the light of the other. By turning the telescope we can see through the slit another colour of both spectra, so that the observation can be effected for each colour. If we have only one source of light for both slits, or if we cause two sources of light of equal brightness to act upon one of the slits, there ensues a slight loss in consequence of the reflection within the apparatus, and the two semicircles are not equally illuminated. If we now interpose a Nicol prism between the telescope and the slit in the diaphragm upon which the spectra fall, we can produce an equal brightness of both fields of vision by turning the Nicol prism. If the sources of light which throw the light into each of the two slits are of different intensity, we can have an equal intensity by another rotation of the Nicol prism. The proportion of the illuminations can be deduced from the angle of deflection.—*Annalen der Physik und Chemie*, and *Zeit. für Analytische Chemie.*

ON THE INFLUENCE OF SALTS UPON THE BEHAVIOUR OF INVERT-SUGAR WITH THE ALKALINE SOLUTION OF COPPER.

By ARTHUR BORNTRAGER.

The author gives an experimental study of the question whether the presence of salts has any effect upon the determination of invert-sugar by the Fehling-Soxhlet method. He concludes that of the salts which are here concerned those having a neutral reaction with litmus (sodium and potassium chlorides, sodium sulphate and acetate) have no effect upon the reductive power of solutions of invert-sugar, either immediately or on prolonged contact in the cold, or on evaporation.

On the contrary, it appears that the salts having an alkaline reaction with litmus (such as sodium carbonate and phosphate) can, by their mere presence, increase the reductive action of invert-sugar. In the case of soda, it further appeared that a prolonged action in the cold has the opposite effect, decreasing this power. Sodium phosphate has no such effect on prolonged action in the cold, but on evaporation. — *Deutsche Zucker Industrie*, 1894, pp. 1529, 1563.

DETECTION AND DETERMINATION OF CALCIUM CHLORATE IN CHLORIDE OF LIME.

By R. FRESENIUS.

Even in recently-prepared chloride of lime calcium chlorate is often present when the calcium hydroxide exposed to the chlorine contained calcium carbonate. In this case hypochlorous acid is liberated, and is quickly decomposed, with formation of chloric acid. Lunge and Schoch found (*Berichte*, 1887, p. 1477) in a very carefully prepared chloride of lime 0·20 per cent of chlorine in the state of chlorate. In old chloride of lime calcium chlorate is almost always present, as appears from the experiments of Pattinson (*Journ. Soc. Chem. Industry*, 1888). He preserved specimens for a year in twelve small stoppered bottles, each holding 120 grms. at 21·1° and 26·6°, and determined every month the chlorine present in the state of chlorate in one of the bottles. The chlorine present in this state increased from 0·09 to 0·43 per cent in the samples preserved at 21·1°; and in those kept at 26·6° up to 1·37 per cent. The striking circumstance that in the former series the samples examined in April, May, June, and July contained no chloric acid; and in the second series mere traces of chloric acid were found in April and May; and that in the second series, in October 1·45 per cent, in November 1·29, and in December 1·37 of chlorine were found in the state of chloric acid might be due to the manner in which the chloric acid was determined. Pattinson added to the specimen of chloride of lime suspended in water aqueous sulphurous acid, heated to ebullition, added after the expulsion of the chief part of the excess of the sulphurous acid a few drops of nitric acid for its complete elimination, neutralised with calcium carbonate, determined the total chlorine by titration with silver nitrate, and subtracted from this value the sum of the chlorine present in the bleaching state and as a chloride. The small quantity of chlorine present in the state of a chlorate was calculated from the difference; that is, by a method in which the inevitable inaccuracies in the determination of the large quantity of chlorine present in the bleaching state and of the chlorine found as calcium chloride must greatly interfere with a precise estimation of the small quantity of chloric acid.

As the question often occurs to chemists whether a chloride of lime contains calcium chlorate, and if so, what quantity? I have sought to elaborate a simple procedure for its direct detection and determination.

It depends upon the fact that the hypochlorites are decomposed by lead acetate with the simultaneous formation of lead peroxide, whilst chlorates remain unchanged; it is convenient to proceed as follows:—

We grind up finely 20 grms. of chloride of lime with a little water, adding gradually more water, rinse the whole into a litre flask, fill up to the neck, shake up well, allow it to subside, filter through a dry filter-paper, and use 50 c.c. of the filtrate for the detection of chloric acid, or for its determination.

In either case we mix the measured 50 c.c. of the solution in a boiling flask with a solution of neutral lead acetate in some excess. There is formed at first a white precipitate of lead chloride and lead hydroxide, which, in consequence of the action of the hypochlorite upon the lead chloride, becomes yellow and then brown, with liberation of chlorine, and passes into lead peroxide—

$$Ca(ClO)_2+PbCl_2=PbO_2+CaCl_2+Cl_2.$$

When the precipitate has subsided, we add a little more solution of neutral lead acetate in order to be certain that the lead salt is present in excess, and if a further precipitation takes place we add still more of the solution of lead acetate.

We now allow the mixture to stand, preferably in an unstoppered boiling-flask, with frequent agitation, when the odour of chlorine gradually disappears; in part by evaporation, but chiefly by acting upon the excess of lead acetate, forming lead chloride and peroxide and free acetic acid—

$$2Pb(C_2H_3O_2)_2+Cl_2+2H_2O=PbCl_2+PbO_2+4C_2H_4O_2.$$

The odour of chlorine disappears completely in about eight to ten hours.

If it is merely requisite to recognise chloric acid, we filter off the precipitate, remove the lead oxide from the filtrate by adding dilute sulphuric acid in slight excess, filter, mix the filtrate with a small quantity of solution of indigo, and then add, drop by drop, a small quantity of a solution of sulphurous acid in water. If chloric acid is present, it is reduced by the sulphurous acid and the lower oxides of chlorine, or if the reduction has proceeded further the chlorine destroys the indigo blue.

That an excess of sulphurous acid must be avoided is manifest, since in that case the action of the chlorine must be annulled; the chlorine being converted into hydrochloric acid by the decomposition of water and the formation of sulphuric acid.

Of the fact that no chloric acid is formed in the above process I satisfied myself by repeatedly preparing solutions of chloride of lime by mixing chlorine water with an excess of milk of lime, filtering, and treating the filtrate with solution of lead acetate, as above directed. In the solutions of chloride of lime thus obtained no chloric acid was ever detected.

If chloric acid is to be determined quantitatively, we wash the precipitate of lead chloride and lead peroxide until the washing water has no longer an acid reaction. The washings are somewhat concentrated by evaporation, added to the filtrate, the liquid is mixed with a solution of sodium carbonate in slight excess; after some time the precipitate of lead and calcium carbonates is filtered off, washed, evaporated nearly to dryness on the water-bath, introduced into a small flask, and the chloric acid is determined according to Bunsen's method, by heating with concentrated hydrochloric acid, conveying the gases given off into a solution of potassium iodide, and determining the iodine liberated with sodium hyposulphite or by Finkener's modification. Six equivalents of iodine liberated correspond to one equivalent of chloric acid.—*Zeit. f. Analytische Chemie.*

SPECIFIC VOLUME AND THE GENESIS OF THE ELEMENTS.

By C. T. BLANSHARD, M.A.

(Concluded from p. 231).

We will now enquire, though with very meagre data to work upon, what light organic chemistry has to throw on the evolution of the elements, from the point of view of differences in specific volume. All specific gravities are taken at 15° C.

Normal Primary Alcohols.

(Sp. grs. in this list and the next from Meyer and Jacobson, *Lehrbuch der organ. Chemie*, Leipzig, 1893).

Formula.	Sp. gr.	Sp. vol.	Diff.
$CH_3.OH$	0·812	39·70	
			17·37
$C_2H_5.OH$	0·806	57·07	
			16·54
$C_3H_7.OH$	0 817	73 61	
			16·30
$C_4H_9.OH$	0 823	89·91	
			16·20
$C_5H_{11}.OH$	0·829	106·1	
			16·3
$C_6H_{13}.OH$	0·833	122·4	
			16·3
$C_7H_{15}.OH$	0·836	138·7	
			16·2
$C_8H_{17}.OH$	0·839	154·9	
			17·1
$C_9H_{19}.OH$	0·842	171·0	
			17·3
$C_{10}H_{21}.OH$	0·839	188·3	

The differences are nearly constant.

Normal Halogen Esters.

Formula.	Sp. gr.	Sp. vol.	Diff.
$CH_3.Cl$	0·952	52·99	
			17·22
$C_2H_5.Cl$	0·918	70·21	
			15·79
$C_3H_7.Cl$	0·912	86·00	
			15·93
$C_4H_9.Cl$	0·907	101·93	
			15·94
$C_5H_{11}.Cl$	0 901	117·87	
			17·16
$C_6H_{13}.Cl$	0·892	135·03	
			17·58
$C_7H_{15}.Cl$	0·881	152 61	
			16·09
$C_8H_{17}.Cl$	0·880	168·70	

Differences nearly constant; with the exception of the fourth and fifth they alternate.

Normal Fatty Acids.

(Specific gravities from Landolt and Börnstein, *Phys. chemische Tabellen*, Berlin, 1894; except the last four, from Meyer and Jacobson).

Formula.	Sp. gr.	Sp. vol.	Diff.
$H.CO_2H$	1·245	36·95	
			18·60
$CH_3.CO_2H$	1·080	55·55	
			18·75
$C_2H_5.CO_2H$	0·996	74·30	
			17·46
$C_3H_7.CO_2H$	0·959	91·76	
			14·71
$C_4H_9.CO_2H$	0·958	106·47	
			16·28
$C_5H_{11}.CO_2H$	0·945	122·75	
			18·40
$C_6H_{13}.CO_2H$	0·921	141·15	
			16·23
$C_7H_{15}.CO_2H$	0·915	157·38	
			16·64
$C_8H_{17}.CO_2H$	9·908	174·02	
			9·35
$C_9H_{19}.CO_2H$	9·938	183·37	

The differences alternate, except the fourth. Ostwald, in his *Lehrbuch der Alg. Chemie*, vol. ii., Stöchiometrie, p. 360, &c., gives a few such tables; but they differ rather widely from these calculations, nor are they nearly so complete.

To take as an example the fatty acid series; Ostwald gives—

	Sp. vol.	Diff.
Formic acid	41·4	
		22·3
Acetic acid	63·7	
		21·7
Propionic acid.. ..	85·4	
		21·7
Butyric acid	107·1	
		23·6
Valeric acid	130·7	

According to Ostwald, and all other observers hitherto, the specific volumes of organic compounds are regarded as rising by constant increments; or, in other words, the differences between the specific volumes are regarded as approximately constant.

But we have seen that, whilst in the case of the normal primary alcohols the differences are nearly constant, there is a more marked alternation of differences in the chlorinated and oxidised series of compounds. Further, we shall find in certain fatty acid esters, and in certain aromatic series, whether chlorinated or not, the same alternation noticeable.

Normal Acetic Esters.

(Specific gravities from Landolt and Börnstein).

	Sp. gr.	Sp. vol.	Diff.
Methyl acetate ..	0·956	77·39	
			20·59
Ethyl ,, ..	0·898	97·98	
			14·11
Propyl ,, ..	0·910	112·09	
			20·18
Butyl ,, ..	0·877	132·27	
			12·82
Amyl ,, ..	0·896	145·09	

We learn from these tables of specific volumes, the most representative that I have been able to collate, that —1. Organic groups behave like the *a* and *b* groups of the elements, having their first differences high; 2. Except the fatty acid series and the chloro-benzene series.

Normal Benzene Hydrocarbons.

(Specific gravities in this and the next Table are from Beilstein, *Handbuch der organ. Chemie*, Hamburg and Leipzig, 1895).

Formula.	Sp. gr.	Sp. vol.	Diff.
C_6H_6	0·884	88·21	
			17·42
$C_6H_5.CH_3$	0·871	105·62	
			16·78
$C_6H_5.C_2H_5$	0·866	122·40	
			15·53
$C_6H_5.C_3H_7$	0·870	137·93	
			17·17
$C_6H_5.C_4H_9$	0·864	155·10	
			16·21
$C_6H_5.C_5H_{11}$	0·864	171·31	

The differences alternate, except the first.

Chlorobenzenes.

Formula.	Sp. gr.	Sp. vol.	Diff.
$C_6H_5.Cl$	1·126	99·87	
			11·42
$C_6H_4.Cl_2$, 1.2	1·320	111·29	
			13·96
$C_6H_3.Cl_3$, 1.2 4 ..	1·465	125·25	
			5·4 ?
$C_6H_2.Cl_4$, 1.2.3.4 ..	—	—	
$C_6H.Cl_5$	1·842	135·86	

It is intelligible that in a highly oxidised series like the fatty acids, or a highly chlorinated one like the chlorobenzenes, the specific volumes should be strongly modified by the chlorine or oxygen respectively.

When I began this article—which has involved many hours' work—I had hoped to be able to demonstrate the greater or less degree of complexity of the so-called elements by comparison with specific volumes of organic substances of known amounts of complexity; but no such conclusions have been arrived at. I hope, however, that my partial success in the solution of this question may lead other workers into the field.

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Continued from p. 232).

Relations between the Concentrations in the Gaseous and Liquid Phases.

The relations between the concentration in the gaseous and liquid phases is clearly shown by curves drawn in a system of co-ordinates, of which the axis of abscissæ is taken for the representation of the molecular percentage composition of the liquid phase, and the axis of ordinates for that of the gaseous phase. These curves are drawn in the figure, the data being taken from the first two columns of tables.

As is seen, the curves prove to be very regular, and group themselves on either side of the diagonal of the square, according as the component chosen to increase from left to right in the diagram is more or less volatile than the other; as this was taken to be the component containing a halogen, the curve is below the straight line when the halogen-containing liquid is less volatile than the other, and above when it is more volatile.

Furthermore, the greater the difference in the volatility of the two liquids in the mixture the greater the curvature. It is very probable that mixtures of two normal

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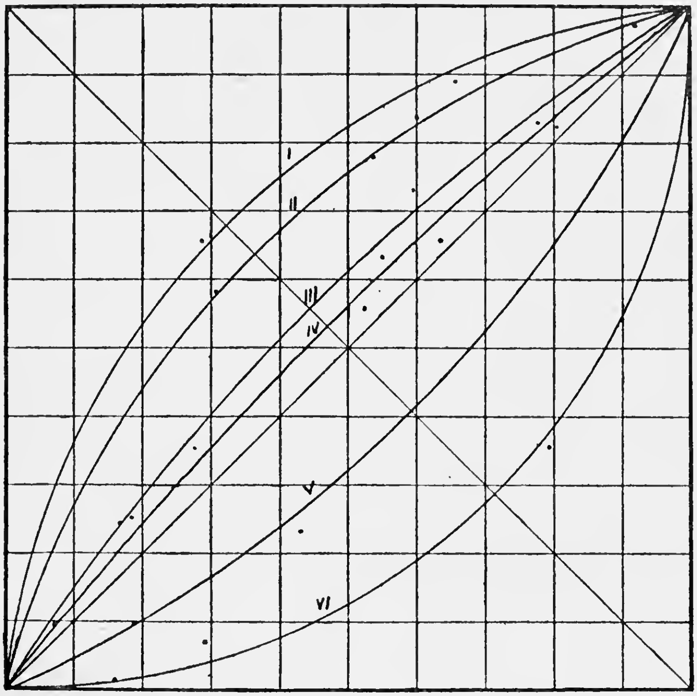
* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.



Relations between the Concentrations in Liquid and Gaseous Phases.

liquids with the same vapour tension would give off vapours with identical composition in both liquid and gaseous state.

Description of the Figure.

Abscissæ = molecules of one liquid in 100 molecules of mixture of liquids.
Ordinates = molecules of one vapour in 100 molecules of mixture of Vapours.

Curve I.	Toluene-chloroform.
,, II.	Toluene-carbon tetrachloride.
,, III.	Benzene-chloroform.
,, IV.	Benzene-carbon tetrachloride.
,, V.	Toluene-monochlorbenzene.
,, VI.	Benzene-monochlorbenzene.

(To be continued).

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 227).

On the Holders used for Freeing Bodies meant to be Volatilised, from Accidental Contamination by Sodium.

I placed on sheets of platinum, or on plates of purified carbon, plane or concave, fixed horizontally, the metallic compounds on which I wished to turn a *hydrogen and air*, *coal-gas and air*, *oxyhydrogen*, or *oxy-coal-gas* blowpipe jet, to free them from accidental sodium impurities. When coming to each case in particular I shall mention, with necessary details, the measures I took for attaining this end. I will say, however, that the heat and draught produced by the flame of a hydrogen and air or an oxy-coal-gas blowpipe are amply sufficient to completely eliminate the sodium; that the pressure of gas *inside* the blowpipe ought never to be more than *four c.m.* of water, and that as a general rule a pressure of *two c.m.* is ample. When one exceeds a pressure of 4 c.m., as is almost always the case when using air delivered direct from a water-pump, the current carries away with it disintegrated particles of the compound, and involves thus the loss of the greater part of the body being purified.

When one uses a hydrogen and air or coal-gas and air blowpipe, the gases ought to be fed from *gasometers counterweighted* to exert the constant pressure wanted.

The same remark applies to oxyhydrogen and oxy-coal-gas blowpipes, when they are used either to eliminate the sodium contained in compounds being experimented on, or to volatilise them for the purpose of making a spectrum analysis of the flame saturated with their vapour.

On the Holders used for introducing Compounds into Flames, Electric Sparks, Electric Discharges, and Electric Arcs.

I necessarily had to adapt holders to the various conditions I had to satisfy. I will now describe shortly the arrangements I made with this object.

A. *On the Clips used to introduce and Volatilise Compounds in Flames whose Temperature is* LESS *than the Melting-point of Platinum.*—When it is required to introduce a compound to be vaporised into the flame of a Bunsen lamp, or into hydrogen burning in air, or into a *vertical* flame of a hydrogen and air or coal-gas and air blowpipe, I used an ordinary holder; that is to say, a very fine pure platinum wire, with the end simply turned up into a hook, or ending in a loop 2 or 3 m.m. diameter, or in a truncated spiral; but when I forced the jet of hydrogen burning in air, or of hydrogen and air, or of coal-gas and air, on to a compound to saturate the jet with its vapour, I placed the compound on a thin, plane or concave, plate of pure platinum. If the compound were *friable* and *infusible*, I collected it into a conical heap from 5 to 10 m.m. high, on a plane platinum sheet, and having made the jet *horizontal* I forced it on to the apex of the cone; when the compound was *fusible*, whether *decomposable* or *not* by heat, I used a very concave sheet of pure platinum. In the centre of the hollow I put a cone of *very porous* pure spongy platinum. The apex of the cone was from 5 to 6 m.m. above the plane surface of the platinum sheet. After having made the platinum sheet and the cone of spongy platinum red-hot, to get rid of accidental sodium impurities, I poured the melted compound on which I wished to operate over the cone, so as to completely saturate it. I then forced the jet against the apex of the cone, taking care to begin with the point of the flame and end with the hottest part.

B. *On the Holders used to introduce and Volatilise Compounds in Flames whose Temperature approaches or equals the Fusing-point of Platinum.* — The dark flame of hydrogen made *incandescent* by the introduction of oxygen, *without forming in it an inner cone*, and the deep blue flame of coal-gas made light blue by the introduction of oxygen, without making an inner cone, have the temperature mentioned above. For introducing a compound into these blowpipe flames, *when vertical*, I used a fine wire of pure platinum or of iridio-platinum containing 20 per cent of iridium, ending in a loop, and both overlaid with pure iridium, so as to stand a temperature considerably above the melting-point of platinum. The iridio-platinum wire was made in 1878, by Mr. George Matthey, for the use of the International Committee on Weights and Measures. The iridio-platinum alloy containing 20 per cent of iridium is as malleable and ductile as pure platinum.*

I succeeded in plating the platinum and the iridio-platinum wire with a suitable coating of white iridium, perfectly adherent and partially combined with the platinum and iridio-platinum, by powdering the wire—first moistened with glycerin—with iridium-black, and then putting it into a coal-gas and air blowpipe jet. By repeating this several times, according to the thickness wished, one can obtain wires ending in a loop or spiral, which stand perfectly well in an oxy-coal-gas blowpipe in which pure platinum wire melts. But if wires thus prepared have the advantage of resisting very high temperatures, they have the disadvantage of being brittle, or of becoming so after use, and of being very difficult to handle without breaking when one tries to make the body to be volatilised adhere to the loop, or to introduce it into the truncated spiral.

Pure platinum wire does not alter the blue flame of a Bunsen burner, but a wire of platinum overlaid with iridium gives it a persistent *violet-blue* tint; this latter wire does not alter the light blue colour of incandescent hydrogen. Spectrum analysis of this last flame shows a continuous spectrum identical with that shown by incandescent hydrogen without an iridium-covered platinum wire—a clear proof that, at this extreme temperature, iridium neither oxidises nor volatilises, as is the case at a lower temperature, just as Sainte-Claire Deville, Debray, and I have found.

One can procure iridium-black suitable for this purpose by reducing chloro-iridiate of ammonium by hydrogen or coal-gas, at the low temperature of the volatilisation of chloride of ammonium, and replacing the hydrogen by pure nitrogen as it cools.

When I had to force a *horizontal* jet of incandescent hydrogen, or the light blue jet of an oxy-coal-gas blowpipe on to a compound, in order to volatilise it, I made different arrangements, according as the body was *fusible* or *infusible*. When the body was *friable and infusible* I made it into a conical heap on a plane sheet of platinum, or on a dish of purified retort carbon; when, on the other hand, the compound was *fusible*, I poured it in a melted state over a cone of very porous spongy *iridium*, placed in a hollow formed in the middle either of a sheet of pure platinum or iridio-platinum, or plate of purified retort carbon, the top of the spongy iridium cone being from 5 to 6 m.m. above the sheet or plate, exactly as I have described above. It is only necessary to substitute a cone of spongy iridium for the cone of spongy platinum used in the former case.

C. *On the Clips used for introducing and Volatilising Compounds in Flames whose Temperature approaches or equals the Fusing-point of Iridium.*—The inner cone of an oxyhydrogen or oxy-coal-gas blowpipe flame, when brought to a minimum length, is at the temperature mentioned above. When I introduced a compound into the interior of the inner cone of a *vertical* blowpipe flame, I completely covered with the compound either a strong filament of purified carbon ending in a sharp point, or a small rod of iridio-platinum with 80 per cent of iridium *forged at white heat*, ending in a fine point overlaid with pure iridium.

When the carbon filament is properly covered with a compound, which remains almost entirely on the surface, it resists, before being completely burnt, a sufficient length of time to permit a spectrum analysis of the flame in which the compound is vaporised.

The small-pointed iridio-platinum rods with 20 per cent of platinum, and overlaid with pure iridium, resist much longer before melting. The pointed end bends when approaching the point of fusion, and thus tells automatically when it is necessary to remove it from the inner cone in order to save it from melting.

When I wished to force the inner cone of an oxyhydrogen or oxy-coal-gas flame, *horizontally*, or nearly so, on to a compound to volatilise it, *without contaminating the holder with sodium*, I met with great difficulties: to overcome these I had to resort to complex methods, which involved me in a long and expensive work, because it necessitated the preparation and employment of very considerable quantities of *pure white iridium*, of welded *iridium plates*, and even of a cup of *fused iridium*.

The first method consisted in the use of a flat plate of pure white iridium, 5 m.m. long, *completely* covering a disc of carbon which had been purified and freed from sodium, 3 c.m. diameter by 5 m.m. thick, let in, to the depth of 6 m.m., to a hole made in a small block of pure magnesia compressed and hardened by being exposed to a white heat, made by the late Colonel Caron. The magnesia block, before receiving the carbon disc, was heated for some time in a coal-gas and air blowpipe, to drive off the sodium obstinately held by magnesia even when it is free from silicic acid.

Having warmed the white iridium plate, which was raised from 2 to 3 m.m. above the top of the block of magnesia, in a coal-gas and air blowpipe, until all the sodium deposited by the air was driven off, I put in the middle of the plate, with platinum forceps, a small iridium dish, which had been welded in an oxy-coal-gas blowpipe flame, carrying either a core of an infusible compound or a hollow core of welded iridium, covered externally with the compound (oxychloride, sulphate, or carbonate) that I wanted to put into the inner cone of an oxyhydrogen or oxy-coal-gas blowpipe, in order to volatilise it and make a spectrum analysis of its vapour.

The second method consisted in replacing the plate of white iridium, permeable by liquids, by a cup of fused iridium, not permeable by liquids, let in for half its height to a small block of pure magnesia, compressed and hardened at a sustained white heat, and heated in an oxy-coal-gas blowpipe until accidental sodium impurities were entirely driven off. The fused iridium cup was 3 c.m. diameter by 8 m.m. high. It was dished in the centre to a depth of 4 m.m., and weighed 102·800 grms. I owe the possession of this unique cup—without which it would have been impossible to raise the vapour of potassium, sodium, and lithium compounds to the temperature of the inner cone of an oxyhydrogen blowpipe flame—to the kindness of Mr. G. Matthey. When I used the cup, a hollow cone of welded iridium was put in the bottom of it. The top of this cone was about 2 m.m. above the edge of the cup. Having raised the cup and the contained cone in an oxy-coal-gas blowpipe flame to

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* "Report of the International Committee on Weights and Measures." Meetings during 1878; Paris 1879.

a temperature near the fusing-point of platinum, I filled it with the liquid compound meant to be volatilised; at the same time I turned the inner cone of an *oxyhydrogen blowpipe flame* on to the top of the cone saturated with the liquid, whilst, with a conveniently placed spectroscope, M. Rommelaere and I proceeded with the spectrum analysis of different parts of the flame charged with vapour. It several times happened that, on turning an oxyhydrogen blowpipe flame on to the top of the iridium cone in the iridium cup containing an alkaline chloride or sulphate heated to the fusing-point of platinum, these compounds exploded, and were thrown to some distance, scattering fiery drops about. To guard ourselves from danger, and to protect our instruments, we covered ourselves and the spectroscopes with wet cloths.

Iridium undergoes no alteration by contact with chlorides and sulphates of potassium, sodium, and lithium, or even lithium oxide, when raised to the highest temperature attainable in an oxyhydrogen blowpipe flame. On the other hand, compounds of calcium, strontium, and barium always attack the surface of iridium, whether welded or fused. It produces thus at first coloured compounds, containing calcium, strontium, and barium. These compounds decompose finally, leaving the iridium with a roughened surface.

I cleansed the articles which had been used in experiments by treating them first with very dilute hydrochloric acid, and then by keeping them for at least one hour in a mixture of equal parts of anhydrous bisulphates of potassium and sodium at a dull red heat. After having washed them thoroughly with water, I heated them in a coal gas and air blowpipe flame, until they showed no trace of the spectrum of the compound which had been in contact with the iridium.

(To be continued).

THE QUANTITATIVE DETERMINATION OF PERCHLORATES.*

By D. ALBERT KREIDER.

The method usually employed for the quantitative determination of perchlorates, by igniting to the chloride and weighing the halogen as the silver salt, is indirect and subject to error, especially as my experience proved, where the free acid is to be determined, and where, consequently, an alkali which is apt to contain chloride is used to form the salt for the ignition. To purify the salt for this method only adds to the complication, and therefore a more satisfactory process was sought. In a recent article (*Amer. Journ. of Science*, vol. xlviii., p. 38) from this laboratory, by Prof, Gooch and myself, a method for the detection of alkaline perchlorates sssociated with chlorides, chlorates, and nitrates was detailed, with mention of certain efforts towards a quantitative determination. As throwing light upon the peculiar properties of perchlorates, and as an introduction to the satisfactory method which I have finally developed, some of the results of these earlier efforts will here be given.

In studying the properties of perchloric acid in the form of its potassium salt, we found that when treated with potassium iodide in the presence of boiling phosphoric acid, no reduction of the perchlorate is effected,—unless indeed, the boiling be continued till the temperature rises to 215° to 220° C., where the meta-phosphoric acid begins to form. But when the meta-phosphoric acid (made by heating the syrupy ortho-acid to 360° C.) is directly applied in the presence of potassium iodide, and kept at a temperature of about 200° C., iodine is copiously evolved. To test this reaction quantitatively, a number of experiments were made in an apparatus consisting of a retort, into the tubulature of which a glass tube was carefully ground and prolonged so as to reach to the bottom of the bulb and serve for the passage of a current of carbon dioxide, used to expel the air and carry the iodine into the receiver. The neck of the retort was bent so as to reach to the bottom of an Erlenmeyer receiving vessel, containing a solution of potassium iodide, which was trapped by a side-necked test-tube. After introducing the perchlorate with the iodide and meta-phosphoric acid, all air was expelled by carbon dioxide and heat applied. The iodine collected in the receiver was titrated with decinormal thiosulphate, from which the perchlorate was calculated.

Table I. gives the results of several experiments performed in this way, which prove that even with a large excess of potassium iodide the perchlorate is so slowly reduced that the hydriodic acid escapes before the reduction is completed. In order to delay the distillation of hydriodic acid until the perchlorate had been completely reduced, the potassium iodide of experiment (3) was introduced in a short tube sealed at one end, so that the meta-phosphoric acid could attack it only slowly, and the heat quickly raised to about 300° C., but evidently without advantage. In experiment (4) the iodide was introduced in the same way, but the heat was applied gradually and more moderately, with considerably improved results.

Table I.

	$KClO_4$ taken. Grms.	$HOPO_2$ used. C.m.^{3}	KI used. Grms.	$KClO_4$ found. Grm.	Error. Grm.
(1)	0·1000	15	5·0	0·0741	0·0259 −
(2)	0·1000	17	10·0	0·0844	0·0156 −
(3)	0·1000	15	5·0	0·0364	0·0636 −
(4)	0·1000	15	5·0	0·0977	0·0023 −

A complete reduction of the perchlorate evidently necessitated the means of introducing the iodide in sufficient quantity and at will.

For this purpose the tube serving for the introduction of carbon dioxide was enlarged so as to hold the iodide, which could then be added to the solution at any time by a manipulation of the rubber conducting-tube for carbon dioxide, which would draw the acid up to the iodide, and, retreating, would carry back an easily regulated quantity of the latter.

Table II.

	$KClO_4$ taken. Grm.	KI used. Grms.	$KClO_4$ found. Grm.	Error. Grm.
(5)	0·1000	5·0	0·0984	0·0016 −
(6)	0·1000	3·0	0·0924	0·0076 −
(7)	0·0500	2·0	0·0508	0·0008 +
(8)	0·0500	2·0	0·0479	0·0021 −
(9)	0·1000	7·0	0·0977	0·0023 −
(10)	0·1000	3·0	0·0925	0·0075 −
(11)	0·1000	3·0	0·0999	0·0001 −
(12)	0·1000	2·0	0·0994	0·0006 −
(13)	0·1000	4·0	0·0966	0·0034 −

Table II. gives a number of results obtained in this way. Experiments (10), (11), and (12) differed from the others only in the employment of a bulb pipette instead of the retort; one end being bent so as to reach to the receiver, and the other cut off rather short with a tube ground into it, serving the same purpose of conducting carbon dioxide and holding potassium iodide—the greater inclination of the potassium iodide tube made possible by this change appearing to offer advantages for the more gradual and regular introduction of the iodide. The amount of meta-phosphoric acid used was in all cases 15 c.m.^{3}. In experiment (13) heat was applied by means of a bath kept at 230°.

While several of these determinations gave only admissible errors, the irregularity of the remainder, and the uncertainty in striking just the proper conditions for good results, proved the method worthless, at least in that shape.

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* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. l., October, 1895.

The experiments of Table III. record the results of adding the acid drop by drop to an intimate mixture of the powdered perchlorate and iodide kept hot.

TABLE III.

	$KClO_4$ taken.	KI taken.	$KClO_4$ found.	Error.
	Grm.	Grms.	Grm.	Grm.
(14)	0·1000	4·0	0·1036	0·0036+
(15)	0·0500	2·0	0·0502	0·0002+
(16)	0·0500	3·0	0·0515	0·0015+

The high results of this Table doubtless point to the dissociation of hydriodic acid or to the partial reduction of the meta-phosphoric acid in the temperature, which would naturally rise higher where so small an amount of liquid was present. But when the meta-phosphoric acid was there in greater amount, the distillation of the hydriodic acid before the complete reduction of the perchlorate could not be prevented.

An ordinary mixture having thus been found insufficient to hold the hydriodic acid to the reduction of perchlorates, a search for some compound in which the perchlorate could be fused with an excess of potassium iodide and the mixture thus obtained subjected to the action of meta-phosphoric acid resulted in the employment of zinc chloride. Anhydrous zinc chloride was found to fuse at about 200° C. The perchlorate and iodide could be added to this fusion, and the whole melted, thoroughly diffused and cooled, without any evolution of iodine. This mass, when treated with meta-phosphoric acid in the apparatus previously employed, melted gradually with a copious evolution of iodine.

Table IV. shows the quantitative action. The amount of zinc chloride used was roughly taken about equal to that of the iodide.

TABLE IV.

	$KClO_4$ taken.	KI taken.	$KClO_4$ found.	Error.
	Grm.	Grms.	Grm.	Grm.
(17)	0·0500	5·0	0·0552	0·0052+
(18)	0·0000	5·0	0·0044	0·0044+
(19)	0·0000	4·0	0·0057	0·0057+

In (19) a mixture of cadmium iodide and potassium iodide, taken in the proportion of their molecular weights, was substituted for the zinc chloride. The known salt corresponding to the formula $CdI_2.2KI+2H_2O$ was not so convenient, because of its high melting-point—230° C.; but when the two iodides are taken in the proportion of their molecular weights, the mixture fuses at about 200° C. Although this mass, after fusion, was more easily soluble than the zinc residue, the blank determination revealed a source of error equally disparaging.

Gaseous hydriodic acid passed into a mixture of the perchlorate and meta-phosphoric acid at a temperature between 200° and 300° C., was markedly less effective than the generation of the acid on the spot; and the distilling of the perchloric acid by meta-phosphoric acid into a receiver of potassium iodide yielded only a trifling amount of iodine, while the passage of hydriodic acid over the fusing perchlorate in a short combustion tube was precluded by the high melting-point of the perchlorate endangering the dissociation of the halogen.

The invariably high results obtained by the use of meta-phosphoric acid in all those experiments in which there was a reasonable assurance that the hydriodic acid was held till the perchlorate was completely broken up—experiments (13), (14), (15), (17), (18), and (19)—indicated either a dissociation of hydriodic acid or a partial reduction of the meta-phosphoric acid. Of the latter cause there were some grounds for suspicion, but, as its determination led too far from the object of the investigation, the use of phosphoric acid was abandoned. So far as our experience extended there remained, then, nothing among the reagents of the wet methods which was sufficiently active and stable enough to warrant its application. Fusion alone seemed capable of extracting the oxygen from the perchlorate. A number of preliminary tests were therefore made on certain salts of the halogens, in the hope of finding one which would be acted upon by the oxygen of the perchlorate with the liberation of the halogen, which latter could be collected in a receiver of potassium iodide and titrated with thiosulphate.

The double chloride of aluminum and sodium, $Al_2Cl_6.2NaCl$, melts at about 200° C., and was in other respects desirable. When fused with potassium perchlorate, chlorine was copiously evolved. The action of air on the fusion also liberated chlorine; but blank determinations in an atmosphere of carbon dioxide proved that under these conditions not a trace of chlorine was evolved. The apparatus employed for a quantitative test of this reaction on perchlorates consisted of a small distilling flask of about 20 c.m.^{3} capacity, into the tubulature of which was ground a piece of glass tubing reaching well into the bulb, and serving for the passage of carbon dioxide. The side neck was sealed to one of two connected Will and Varrentrapp absorption bulbs containing a solution of potassium iodide to receive the chlorine. After weighing the perchlorate into the flask, and adding a sufficient amount of the powdered double chloride, all air was expelled by carbon dioxide, and heat applied till the fused mass was raised considerably above the melting-point and kept there for some time. Table V. contains the results of a number of experiments performed in this way.

TABLE V.

	$KClO_4$ taken.	$KClO_4$ found.	Error.
	Grm.	Grm.	Grm.
(20)	0·0500	0·0438	0·0062−
(21)	0·0500	0·0482	0·0018−
(22)	0·0500	0·0460	0·0040−
(23)	0·1193	0·1175	0·0018−
(24)	0·1039	0·1018	0·0021−
(25)	0·0500	0·0477	0·0023−
(26)	0·1003	0·0946	0·0057−

These results came so close to being quantitative that a little help in the form of free acid seemed all that would be necessary to complete the reaction. But the addition of meta-phosphoric acid to the cooled mass after the fusion in (22) gave no additional evolution of iodine. In (25) gaseous hydrochloric acid was passed in with the carbon dioxide in the hope of meeting the deficiency, but was evidently no improvement. One test, in which meta-phosphoric acid was added to the fusion, resulted in such a violent evolution of hydrochloric acid that the whole contents of the flask was forced into the receivers.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, November 8th, 1895.

Prof. A. W. Rücker, Vice-President, in the Chair.

Mr. W. H. Everett read a paper on "*The Magnetic Field of any Cylindrical Coil or Plane Circuit.*"

The method of treatment is based on the formula for the force due to an element of current. A single integration applied to one component of this force gives for any point in the field due to a plane circuit the force perpendicular to its plane; and a double integration gives the longitudinal force at any point due to a cylindrical coil of any cross-section, the depth of winding being supposed inconsiderable. For coils in which the latter condition does not hold, an approximate solution can readily be found. The force parallel to the plane of a circuit, and the transverse force due to a coil, are investigated in a similar manner. The general results are of a very simple form and admit of easy approximate calculation. Special formulæ are deduced for coils of rectangular cross-section, the general expressions being in this case integrable.

Appended to the paper are some numerical results giving the values of the forces at different points due to coils of various dimensions.

Prof. Perry said he considered the paper to be a valuable one, particularly as illustrating a practical mathematical method of integrating.

Mr. Trotter said the paper was of interest to him, as he considered that several of the author's results might be applied to the solution of problems on illumination, *cf.*, the illumination of a room by a circle of lamps.

Mr. Rhodes regretted that it had not been possible to supply a proof of the paper before the meeting. The method in which the author obtained the force outside a solenoid as the difference of the forces due to two solenoids reminded him of the method employed in calculating the attraction of, say, a truncated pyramid.

Prof. Silvanus Thompson said the author had mentioned several previous papers on the subject, but had not referred to one by Prof. Viriamu Jones, in which the force due to a solenoid is obtained in terms of elliptic integrals. Another method of attack was to calculate the work done when a unit pole is carried through the solenoid and back outside to the starting-point.

Prof. Ayrton said he also regretted the absence of a proof of the paper. He considered it of great importance to have exact and simple methods of calculating the forces due to a solenoid.

The Chairman (Prof. Rücker) said he had made a somewhat similar calculation in connection with the magnetic effect of sheets of basalt below the surface of the earth.

Mr. E. H. Griffiths read a paper, by himself and Miss Dorothy Marshall, on "*The Latent Heat of Evaporation of Benzene.*"

The method employed is similar to that used by one of the authors in the determination of the latent heat of evaporation of water (*Phil. Trans.*, 1895). The loss of heat due to the evaporation is balanced by (*a*) the heat supplied by an electric current; (*b*) a secondary supply due to the work done by the stirrer; (*c*) a slight gain or loss due to small unavoidable changes in temperature of the calorimeter. The comparative values of the various sources of heat (if we denote the supply due to the electrical current by 1000) is approximately:—Electrical = 1000; stirring = 11; changes in calorimeter temperature, ± 5. The electrical supply could be measured with extreme accuracy, and the above table shows that small errors in the determination of the remaining thermal quantities are of little importance. The results may be summed up in the formula—

$$L = 107{\cdot}05 - 0{\cdot}1581\,\theta;$$

where θ is the temperature, and the thermal unit at 15° C. is used.

The discussion on this paper was postponed till after the reading of the following paper.

"*On a Method of Comparing the Heats of Evaporation of different Liquids at their Boiling-points.*" By Prof. Ramsay and Miss Marshall.

The method employed has already been described before the Society (Jan. 11th, 1895). The liquid to be experimented on is put into a glass bulb enclosed in an outer jacket filled with the vapour of the same liquid. An open tube is attached to the top of the bulb, so that there is free communication between the interior and the vapour-jacket, and no loss of material. Inside the bulb is a spiral of fine platinum wire, attached to stout platinum terminals which are sealed into the glass. The temperature of the liquid in the bulb is raised to the boiling-point by the vapour-jacket; thus when a current is sent through the wire the whole of the heat developed is spent in converting a portion of the liquid into vapour. Two such bulbs are connected in series, and the ratio of their losses of weight is the inverse ratio of the heats of evaporation of the liquids. A correction is made for the inequality in resistance of the spirals, and the ratio of the differences of potential between the ends of the spirals, when the current is passing, is determined in each experiment by Poggendorff's method. Results are given for fourteen liquids.

Prof. Ramsay drew special attention to the table giving the values of the quotient $\frac{M\,L}{T}$, where M is the molecular weight, T the absolute temperature, and L the latent heat. Very curious differences are noticeable in the case of water, alcohol, and acetic acid.

Prof. Carey Foster expressed his admiration for the method, since it obviated the necessity of knowing the specific heat of the liquid or vapour.

Prof. Silvanus Thompson said the difficulty experienced in the case of water, due to electrolysis, might be obviated by the employment of a spiral of lower resistance and a larger current, so that the difference of potential between the ends of the spiral should be less than 1·7 volts.

The Chairman said Captain Abney had asked him to enquire to what extent the temperature of the liquid was affected by radiation.

Mr. J. W. Rodger asked if any direct experiment had been made to determine if the temperature of the liquid was not above its true melting-point. In some cases differences of as much as 2° might exist between the temperature of the liquid and that of the vapour given off. The differences in the value of $\frac{M\,L}{T}$ in the case of water, alcohol, and acetic acid might be due to the fact that the vapours of alcohol and water were simple, while the vapour of acetic acid was complex.

Mr. R. Appleyard suggested that the differences obtained in the case of water might be due to the presence of dissolved air.

Mr. Griffiths said that the objection to the adoption of Prof. Thompson's suggestion was the fear that, with short wires, an excessive difference in temperature between the wire and the liquid might exist.

Mr. Rhodes asked if Mr. Griffiths could trust his determinations of temperature to $\frac{1}{80000}$th of a degree?

Mr. Griffiths, in reply, said that he thought there was no limit to the accuracy with which a difference of temperature could be measured; the absolute temperature, however, he only relied upon to $\frac{1}{1000}$th of a degree.

Prof. Ramsay said the fact of superheating existing would not affect the results, since near the temperatures at which they were working the latent heat did not vary appreciably with the temperature. In reply to Captain Abney, he said some previous experiments by Dr. Young and himself had shown that the vapour-jacket was quite impervious to radiant heat from without.

Royal Institution.—The Christmas Course of Lectures, adapted to a juvenile auditory, at the Royal Institution, will be delivered this year by Professor John Gray McKendrick, M.D., LL.D., F.R.S., Professor of Physiology in the University of Glasgow, and formerly Fullerian Professor of Physiology in the Royal Institution. The subject will be "Sound, Hearing, and Speech," and the Lectures will be experimentally illustrated. The first Lecture will be delivered on Saturday, December 28th, at Three o'clock, and the remaining Lectures on December 31st, 1895, and on January 2nd, 4th, 7th, and 9th, 1896.

Illuminating Apparatus for observing the Changes of Colour in Volumetric Analyses.—This apparatus has been constructed by A. Lupp, and can be obtained from Kähler and Martini, of Berlin. In principle it is like an arrangement often employed in dissecting microscopes.

NOTICES OF BOOKS.

Aids to the Analysis of Food and Drugs. By T. H. Pearmain and C. G. Moore, M.A., F.C.S., Members of the Society of Public Analysts. London: Baillière, Tindall, and Cox. Pp. 160.

This little book at once commends itself to our good wishes by its Preface. The authors say:—"This work is not intended to be used as a cram-book for examinational purposes. We cannot emphasise too strongly the fact that food analysis is not to be taught in a few weeks, as is frequently attempted in the interest of public health students. A competent knowledge of the analysis of food and drugs is only to be obtained by some years of active practical laboratory work."

In treating of the analysis of milk, the authors remind us that the disgraceful state of the milk trade in this country is fostered, if not actually created, by the "absurdly low standard" adopted by the Somerset House chemists who have been constituted the referees in adulteration cases. They have fixed upon 2·75 per cent as the minimum for fat, and 8·5 for "solid not fat." If we compare this standard with that adopted elsewhere, we find that it is exceptionally low. The State of New York requires fat 3 per cent; New Jersey demands total solids 12; in Massachusetts the standard is 13 solids; and in Berne total solids 12·5, and fat 3·5.

But there are other, and not less grave, errors in the "Sale of Food and Drugs Act." Its scope needs to be enlarged, so as, *e.g.*, to bar the way to such quibbles as the well-known plea that baking powder was neither food nor a drug. The penalties are most absurdly low, and have merely a maximum limit which magistrates can and do at times reduce so as to render the punishment of the sophisticator practically *nil*.

In the matter of vinegar the authors seem to participipate in the common English notion that this condiment should be made from malt. Now the nitrogenous matter in malt or other grain cannot at all contribute to the production of vinegar. It seems not improbable that the presence of dextrine tends to prevent the formation of those ethers which constitute the aroma of wine-, cider-, and sugar-vinegars. This theory, which merits experimental investigation, would account for the flatness of malt-vinegar.

As regards pepper, it would be well if the importation of "poivrette" and of its raw material—to wit, olive-stones—were totally prohibited. The estimation of the woody fibre seems to be a capital point in the analysis of peppers. The presence of lead chromate in any substance intended for introduction into the human system is a crime for which no money penalty is at all adequate.

The analytical procedures here recommended are trustworthy, and indicate that the authors are not compilers, but men of experience.

The Splash of a Drop. By Prof. A. M. Worthington, M.A., F.R.S. Being the Reprint of a Discourse delivered at the Royal Institution of Great Britain, May 18th, 1894. Published under the Direction of the General Literature Committee. London: Society for Promoting Christian Knowledge. 1895. Crown 8vo., pp. 76.

The curious work before us discourses on the phenomena observed when a drop of water falls into milk; of a drop of mercury falling upon a hard, polished surface; and of a drop of milk falling upon smoked glass. The author treats only of the mechanical phase of the question, leaving, for the present at least, the electrical aspect to other investigators, such as Lenard and J. J. Thomson. As to any possible chemical phenomena produced, the author is silent.

Prof. Worthington has succeeded in reproducing the effects produced by means of the instantaneous photographic process. Thus the illustrations show, *e.g.*, the appearances respectively 0·0262, 0·0391, and 0·101 second after the contact of a drop of water with a surface of milk. Some of these figures decidedly remind us of the lunar craters as seen with the telescope.

Principles and Practice of Agricultural Analysis. A Manual for the Estimation of Soils, Fertilisers, and Agricultural Products. For the Use of Analysts, Teachers, and Students of Agricultural Chemistry. Volume II.—*Fertilisers.* By Harvey W. Wiley, Chemist of the U.S. Department of Agriculture. 8vo., pp. 332. Easton, Pennsylvania: Chemical Publishing Co. 1895.

The appearance of this work is a striking proof of the great and enlightened attention paid to agriculture by the Government of the United States. The author's object has been "to present to the busy worker a broad view of a great subject" Those who merely want a book for routine work or in preparing for an examination are warned that they will here find little to attract them.

The present volume comprises four parts. The first treats of phosphates and phosphatic manures; the second is concerned with nitrogen in manures and their components; the third discusses potash as a manurial constituent; and the fourth speaks of such minor fertilising materials as lime, gypsum, common salt, copperas, and wood-ashes.

It will be at once seen that Mr. Wiley, like most British agricultural chemists, but unlike an eminent French authority, is far from placing lime in any form in the same rank as the three great plant foods—nitrogen, phosphates, and potash. Whilst giving the general preference to the molybdic method, Mr. Wiley points out certain sources of error which must be avoided; such as the occlusion of silica. One method of evading this difficulty is dissolving the original substance in sulphuric acid with a little nitric acid. Silica is not soluble in hot concentrated sulphuric acid. Error may, though rarely, arise from the presence of arsenic, and more frequently from the occlusion of magnesia and the volatilisation of phosphoric acid.

Basic phosphoric slags have come into such extensive use that they have attracted the notice of sophisticators. Hence their analysis, and the detection of adulterations (some of which have been actually patented!), becomes an important question. It must be noticed that the substance known in Europe as Thomas slag is called in America "odourless phosphate."

For the determination of nitrogen in manures and their crude materials, the author gives the process of Dumas, available in all cases, but now rarely used except as a check; the soda-lime process of Varrentrapp and Will, very generally used until of late for the determination of nitrogen not in the nitric form; and the Kjeldahl method, also not available for nitric nitrogenous bodies. The process of Wanklyn is pronounced to be of no practical use whatever.

For the detection of potash in manurial matters, we find mention of a spectroscopic method. Potassium gives three faint and rather broad bands, two red bands, and one of a plum colour. If these bands are not detected, we may at least conclude that the substance does not contain a ponderable quantity of potash. In addition to the ordinary platinum chloride method for the determination of potash in its various modifications, we find the process for its estimation as perchlorate, which is pronounced quite as accurate as the platinum process, simpler, more expeditious, and cheaper.

Mr. Wiley expresses the hope that deposits of potassium salts may be discovered in the United States.

The fourth part of this excellent work treats of miscellaneous fertilisers. The author considers—in our opinion, rightly—that a soil good enough to grow crops will contain sufficient lime to furnish that ingredient of plant food for many years. The action of lime is certainly most favourable to those plants which are of value to men, whilst the plants which avoid lime, though often very beautiful, such as the heaths, azaleas, &c., are of little economical value.

We are struck with a passage to the effect that lime is not capable of acting as a fungicide. "As a rule fungi prefer acid reaction in the substances in which they grow." With the morbific microbia this rule hardly applies. Most disease germs seem to prefer an alkaline medium. Thus the use of liquids containing a trace of sulphuric acid seems a safeguard against the infection of Asiatic cholera. Yellow fever, on the contrary, prefers an acid habitat.

Gypsum, it appears, has the strange synonym of "land-plaster."

Under the name "Stall manures," the author includes farmyard manures, night-soil, the excreta of poultry, &c. Mr. Wiley very truly declares that such manures have a higher manurial value than is deducible from the proportions of phosphorus, nitrogen, and potash which they contain (p. 311). This opinion we can confirm from our own observations, and we must regret that it has been ignored by many authorities in pronouncing on the value, *e.g.*, of sewage manures.

Mr. Wiley's work must be regarded as a splendid contribution to the chemistry of agriculture.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 18, October 28, 1895.

Lord Kelvin, as a Foreign Associate of the Academy of Sciences, read the Address of the Royal Society of London congratulating the Institute of France on its centenary, and further delivered a speech recognising France as his *alma mater* of science.

On the Chemical Equivalents.—M. Margfoy.—The actual equivalents of chemistry are the prime numbers comprised in the natural series of whole numbers between 1 and 300. The author gives a table of his new equivalents in columns parallel with the present equivalents and the atomic weights. The equivalents of boron and sulphur he makes identical, as also those respectively of magnesium and glucinum, of chrome and palladium, of tin and cobalt. That of nickel he makes 149, as against the equivalent 29·5 at present accepted. Gold and platinum he makes alike, as also tungsten and lanthanum, and iridium and osmium. The number of prime numbers which exist among the 300 whole numbers is 63. M. Margfoy adds that he has established the constitutive theory of substances founded on the unity of matter, he introduces into the consideration of the volumes the element of porosity, and thus succeeds in combatting the law of Dulong and Petit and the hypothesis of Avogadro. He puts forward the following law:—The specific heat multiplied *by the density is equal to the porosity*, the porosity of hydrogen under the existing conditions of temperature and pressure being taken as unity.

Thermo-chemical Researches on Lithium, Magnesium, and Copper Cyanides.—Raoul Varet.—The author's results are that the heat evolved from Li in solution with gaseous cyanogen and water is +65·12 cal.; that from magnesium under the same conditions is +112·0 cal.; and that for copper +29·8 cal.

Glucinum Carbide.—Louis Henry.—If we ascribe to glucinum the atomic weight 9·03, and to carbon that of 11·97, glucinum carbide must be represented by the formula CGl. Lebeau's investigation gives us no reason for modifying the atomic weight and the valence generally attributed to glucinum.

Analysis of Emerald.—P. Lebeau.—The author has operated on the emerald of Limoges (Chanteloube, Haute Vienna). He gives the following results:—

	I.	II.
Loss at a red heat	1·46	1·41
Silica	66·06	65·80
Alumina	16·1	16·40
Glucose (? should be glucina)	14·33	14·21
Ferric oxide	1·2	0·9
Mn_3O_4	—	—
Magnesia	0·55	0·61
Lime	0·17	0·14
Phosphoric acid	0·11	0·09
Alkalis	—	—
Titanic acid	traces	traces
	100·11	99·67

Determination of Argon.—Th. Schlœsing, jun.—This paper will be inserted in full.

Synthetic Formation of a New Ketonic Acid.—E. Burker.—The compound in question has been obtained by the action of camphoric anhydride upon benzene in presence of aluminium chloride. Its composition is $C_{15}H_{20}O_2$. It forms white crystals of a nacreous lustre which melt at 135—137° and boil at 320° at a pressure of 760 m.m. They are almost insoluble in water, sparingly soluble in ligroine, but readily soluble in acetic acid, alcohol, ether, benzene, chloroform, and carbon disulphide. The author has formed and examined its ammonium, barium, silver, copper, cobalt, nickel, zinc, and lead salts. He has also obtained its ethylic and methylic ethers, its anhydride, amide, and hydrazide.

Liquefaction of Gelatin; its Saline Digestion.—A. Dastre and N. Floresco.—Gelatin is transformable into a kindred substance, gelatose or protogelatose, characterised by want of the property of forming a jelly and of being precipitated by a standard solution of sodium chloride. In cultures of liquefactive microbia it is observed in the first moments that the gelatin is changed into gelatose. Gelatin loses the property of jellifying if left in contact with an alkaline chloride or iodide. With the fluorides, the transformation is only partial. The change may be named saline digestion.

Zeitschrift fur Analytische Chemie.
Vol. xxxiv., Part 2, 1895.

Researches on the Amorphous Nitrogenous Organic Compounds present in Beer Worts.—H. Schjerning.

Determination of Sulphurous and Sulphuric Acids in the Products of the Combustion of Coal-gas.—Uno Collan.—The author hopes to have demonstrated that the sulphur of coal-gas, both in the luminous and in the non-luminous flames, is chiefly converted into dioxide.

Demonstration of the Blood-spots in Judicial Investigations.—M. Gantter.—(See vol. lxxi., p. 238).

Improvements in Glass Cocks.—H. Wolpert.—This paper requires the nine accompanying figures.

Retardation of Ebullition, and on the Ejection of Liquids.—H. Wolpert.

New Burner for Sodium Light.—Richard Pribram.

Simple Apparatus for Extraction.—Richard Pribram.

Apparatus for Measuring off Small Quantities of Mercury in the Kjeldahl Nitrogen Process.—Paul Liechtli.—These three above papers cannot be intelligibly reproduced without the accompanying figures.

Determination of Antimony as Antimonic Antimoniate.—Otto Brunek.—Already inserted.

Examination of Butter.—Carl Th. Mörner.—The author finds the baryta number for twenty samples of fresh butter from Central and Southern Sweden on the average 200·7, *i.e.*, a little lower than the values obtained by König and Hart.

Introduction to Microchemical Analysis.— H. Behrens.— This work is noticed in a brief but highly laudatory manner.

Use of the Electric Current as a Source of Heat.—A conspectus of the methods devised by Saladin (*Soc. Chim. de Paris*), Ducretet and Lejeune (*Ibidem*), H. Moissan, Jules Violle, and Lagrange, and Hohe (*Comptes Rendus*).

Sources of Current, Resistance, and General Arrangements for Electrolysis.—A compilation including notices of a new dynamo for metallurgical laboratories and lecture rooms, by W. Borchers (*Comptes Rendus*).—As the most convenient source of electricity for chemical laboratories Karl Elbs (*Chemiker Zeitung*) recommends accumulators which may be readily charged by a Gülcher thermo battery of 66 elements. Felix Oettel (*Chemiker Zeitung*) shows that in directions for the electro-deposition of metals it is necessary to specify the strength of the current per unit of surface; as such unit he selects the square decimetre. Communications follow by J. S. Stillwell and Prof. P. T. Austen on the use of electric lamps in electrolysis. The authors use glow-lamps as resistances, which, as the Editors point out, is no novelty. The contents of Rüdorff's paper are purely polemical.

Use of Sound Vibrations in the Analysis of Gaseous Mixtures.—E. Hardy.— From the *Comptes Rendus.*

Apparatus for Purifying Oxygen and Air in Elementary Analysis.—Hugo Schiff —A description of the apparatus would require the two accompanying figures.

New Urometer.—Th. Lohnstein (*All. Med. Central-Zeitung*).—A special form of hydrometer.

Some small Laboratory Apparatus.—André Bidet.—These appliances cannot be satisfactorily described without the accompanying figures.

Motor for Laboratory Purposes.— Ewald Saur.—This apparatus is an application of Henrici's hot-air motor, and cannot be described without the illustration here given.

New Cock for Vacuum Exsiccators.—O. Ernst.

Determination of Carbon in Iron.—A critical compilation of known methods.

Distinction between α- and β-Naphthols.—Aymonier (*Repert. Pharm.* and *Zeit. des Allgem. Oesterr. Apotheker Vereins*) uses a solution of 1 grm. of potassium dichromate and 1 grm. nitric acid in 100 c.c. of distilled water. If a few drops of this solution are added to an aqueous or dilute alcoholic solution of the naphthols there appears a black precipitate in the absence of α-naphthol.

MEETINGS FOR THE WEEK.

Wednesday, 20th.—Society of Arts, 8. Opening Address of the 142nd Session, by Major-General Sir John Donnelly, K.C.B., Chairman of the Council.

Thursday, 21st.—Chemical, 8. "The Evolution of Carbon Monoxide by Alkaline Pyrogallol Solutions during Absorption of Oxygen," by Prof. Clowes. "The Composition of the Limiting Explosive Mixtures of various Combustible Gases with Air." "Barium Butyrate, and the Estimation of Butyric Acid," by W. H. Willcox. And other papers.

Friday, 22nd.—Physical, 5. An Exhibition of Photographs of Spectra, by G. Johnstone Stoney. "A Direct-reading Platinum Thermometer," by R. Appleyard. "Historical Note on Resistance and its Change with Temperature," by R. Appleyard.

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THE CHEMICAL NEWS.

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ON ARGON.

By R. NASINI.

The author is of opinion that the monatomic character of argon, as deduced from the kinetic theory of gases, cannot yet be regarded as irrefragably established. If the kinetic theory of gases allows us to predict for monatomic gaseous molecules with great probability a value for k approximating to 1·67 (k being the relation of the specific molecular heat at a constant pressure to the specific heat at a constant pressure), according to the author, the reciprocal relation is not to be regarded as necessary; that is, it cannot be generally concluded that k has the same value for every monatomic molecule. It is sufficient to assume that the energy of the rotatory movements represents a very small and negligible part of the progressive movements, and that no—or only very slight—movements take place between the several atoms within the molecule in order to justify the assumption that also in polyatomic gaseous molecules the value 1·67, or an approximate number, can be obtained for k. If, further, the value 40 were absolutely demonstrated as the atomic weight of argon, this element would find no place in the periodic system, and the system itself would be subverted; as would also be the case if a value were found for tellurium higher than that for iodine.

If we assume the value 20 for argon, it may find a place in the 8th group between fluorine and sodium. This place in the periodic system seems very suitable, especially as the transition from fluorine to sodium is not at all mediated. If, according to the conjecture of the discoverers, argon consists of two elements with the atomic weights 37 and 82, we could no longer admit the eighth group in the sense now admitted. It would then be necessary to assume the existence of a new element after each halogen, so that, *e.g.*, an element of the atomic weight 20 would follow after fluorine, and another between iodine and cæsium. These elements would then form an eighth group and conclude the period, whilst the present eighth group must form a new group—the ninth.

In the present position of the question we must abandon either the conclusions universally deduced from the kinetic theory of gases or the periodic system.

As long as more cogent evidences cannot be brought forward, the author does not believe that 40 represents the true atomic weight of argon.—*Gazz. Chim. Italiana* and *Chemiker Zeitung.*

ON THE DETERMINATION OF ARGON.

By TH. SCHLŒSING, Jun.

The procedure for the determination of argon described in my last paper (*Comptes Rendus*, cxxi., No. 16; Chem. News, lxxii., p. 211) yields, according to the verifications submitted, results too low by an average of 0·6 per cent. This error is not great; we know its direction and we may accept it. I have sought to ascertain its cause, not so much in order to arrive at a closer approximation, as in the hope of detecting some reaction which is the origin of the slight loss observed.

In the apparatus which I have described, argon is brought in contact at a red heat with magnesium, copper, cupric oxide, steel, porcelain, and asbestos. Can it be some one of these substances which has a slight action upon argon? In order to answer this question I have performed a methodical series of experiments, causing volumes of argon, accurately measured, to circulate in the apparatus for a certain time, then extracting them, and re-measuring them after having been submitted to the spark in presence of oxygen and potassa, the conditions of the experiment having been successively modified, so that we may perceive the influence of each.

These experiments, which it would be too tedious to describe in detail, have shown that the total of the somewhat complex manipulations of a determination involves a small loss of about 0·25 per cent of argon, when the magnesium tube has not been heated; that the total loss is between 0·5 and 1 per cent if the tube is heated as for an ordinary operation; that it increases slightly with the duration of the experiment, and also with the tension of the argon in the apparatus; and that it does not appear distinctly due either to the steel, the porcelain, the asbestos, the copper, or the cupric oxide. It followed already from the experiments of Lord Rayleigh and Prof. Ramsay that argon is not appreciably absorbed by copper or by cupric oxide, and here the fact is verified with all needful precision.

Among the experiments which I mention, those in which the tube of steel or of porcelain is heated, as in the majority of the determinations, for an entire hour have given the following losses:—0·70, 1·13, 0·66, 0·69, 0·63, 0·43, 0·51, or a mean of 0·68 per cent of the argon. This figure, 0·68 per cent, agrees well with that (0·62) of the experiments of verification referred to above. In fine, we may admit that for a series of determinations the mean error is approximately 0·7 per cent.

I have applied the procedure in question to the determination of argon in normal air. It has given the following results:—

Normal Air taken in Paris at about 10 *metres above the Ground.*

	Argon	
	In 100 vols. of atmospheric nitrogen.	In 100 vols. air containing 79·04 of nitrogen.
Sept. 25	1·185	0·9369
„ 26	1·183	0·9349
„ 30	1·185	0·9367
Oct. 1	1·180	0·9325
„ 4	1·185	0·9363
Mean..	1·184	0·935

	In 100 vols. of atmospheric nitrogen.	In 100 vols. of air.
Air taken in Normandy, on a hill of 305 metres high	1·182	0·9343
Air taken at 300 metres high on the Eiffel Tower	1·180	0·9328
Air taken in an iron mine	1·183	0·9354
Mean..	1·182	0·934

The slight respective differences shown by these results are of the rank of experimental errors. They do not necessarily correspond with real variations of the amount of argon in the air. If such variations occur they are probably very slight. Thus it must be laid down for argon as for the two most abundant elements of the atmosphere, oxygen and nitrogen, its proportion varies only to a degree scarcely perceptible on analysis. The constant composition of our atmosphere is explained, as it is known by the incessant stirring to which it is submitted. As regards argon, its chemical inactivity, if confirmed, would be another reason why it should not vary.

If we make the correction of 0·7 per cent in addition to the above means as regards normal air they become 1·192 and 0·941. We may easily calculate the difference with this figure of 1·19 per cent (the first cause of the discovery of argon) between the weight per litre of atmospheric nitrogen and that of chemical nitrogen—a difference which Lord Rayleigh and Professor Ramsay determined directly by measurements of great precision, and found equal to 1·2572 grm. − 1·2505 grm., or 0·0067 grm. If, in fact, D_1, D_2, and D_3 are respectively the weights per litre of argon, of chemical nitrogen, and of atmospheric nitrogen we should have—

$$0{\cdot}0119\ D_1+(1-0{\cdot}0119)\ D_2=D_3,$$

whence—

$$D_3-D_2=0{\cdot}0119\ (D_1-D_2).$$

Now, the experiments of Rayleigh and Ramsay show us D_1 and D_2. They have given $D_2=1{\cdot}2505$ grm., and for the density of argon with reference to hydrogen 19·9, or for the weight per litre $19{\cdot}9\times 0{\cdot}0896$ grm., or 0·783 grm. We have, therefore, with a sufficient precision $D_1-D_2=0{\cdot}5325$ grm. and $D_3-D_2=0{\cdot}0063$ grm. This value of 0·0063 grm. of the difference in question ought to be, in consequence of the procedure by which it is obtained, a closer approximation than the foregoing 0·0067 grm.

Here follow some results referring to gases extracted from agricultural soils.

	Argon for 100 vols. of nitrogen accompanied with argon.
Gas taken at a depth of 0·20 metre in the soil of a pine forest	1·170
Gas taken at a depth of 0·40 in a ploughed soil..	1·169
Gas taken at a depth of 0·40 in a ploughed soil..	1·155
Gas taken at a depth of 0·40 in the soil of a garden	1·118

The mean of these figures is lower than that corresponding to normal air, which depends in part on the solvent action of water (argon, according to Rayleigh and Ramsay, about 2½ times more soluble in water than is nitrogen), always supposing that the rain reaches the soil before it has taken up from the air all the proportion of argon which it can dissolve.—*Comptes Rendus*, cxxi., p. 604.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 241).

D. *On the Holders used to hold Compounds in an Electric Spark or Discharge.*—To hold the compounds to be volatilised I used platinum or iridium balls 3 m.m. in diameter, at the end of a platinum wire 1 m.m. in diameter, or, better still, small cones of purified carbon fixed to a platinum wire. The platinum or iridium balls, and the small carbon cones, were *completely* covered with the compounds in the form of *anhydrides* or hydrates, or sometimes merely soaked in a saturated solution of the compound to be volatilised.

I made different arrangements according as I passed the spark or current in the *surrounding air*, or in *purified air*, or in *pure hydrogen*.

When I worked in the outer air I clamped, and held by screw clips, the platinum wires, ending in balls or small carbon cones covered with the compounds, between two separate and insulated metal rings. The two metal rings were attached to a varnished glass stem by means of insulated supports. The glass stem was mounted on a metal stand; it could be raised or lowered by means of a rack with which the stand was furnished. Thanks to these arrangements, one could raise to any height required the two rings attached to the stem, adjust the distance between the balls or saturated carbon cones, and pass the spark or discharge between them.

Having arranged the apparatus in front of, and as near as possible to, the slit of the spectroscope, and having guarded it against spattering by interposing a thin sheet of mica, one can at will let through the slit of the spectroscope the rays from either the middle of the spark or from either of its ends.

When the platinum balls or the carbon cones were completely covered by the compounds to be volatilised, spectrum analysis of a spark, or even a discharge, showed no lines due to platinum or carbon.

When working in *purified* air, or, better still, in *pure* hydrogen, I used the same platinum wire holders, ending in balls of this metal or of iridium, or carbon cones, completely covered with the compounds to be volatilised in the spark or discharge; but in this case I arranged the platinum wires by means of well-washed corks in a glass tube open at both ends, from 2 to 3 c.m. diameter by 10 c.m. in length.

At a distance of 2 c.m. from each end was fixed a small glass tube, furnished with a cock meant to admit and maintain a current of purified air or pure hydrogen whilst the sparks or electric discharges were passing.

Whatever care might be used in fitting the apparatus, it was impossible to prevent the outer air from diffusing into the gas in the tube, especially when this gas was hydrogen. For this reason it was necessary to maintain the current during the experiment, and at least to *completely* cover the corks fitted to the tube, as well as a part of the tube itself, with a layer of melted shellac or wax.

When working with a *spark* in the open air I sometimes did and sometimes did not see atmospheric lines. In a note* I give the reason of the *appearance* and *disappearance* of atmospheric lines.

Spectrum analysis of the *discharge* in air enabled me to detect *the constant presence* of atmospheric lines superposed on the lines of the compound volatilised in the discharge. This constant presence makes observations of a discharge painful and uncertain.

Passing a short spark in hydrogen showed only the red hydrogen line with the spectrum of the volatilised compound, whilst a discharge in hydrogen constantly shows the red and bluish green C and F lines superposed on the spectrum of the volatilised compound, the F line appearing as a band shaded on both sides. However intense the discharge might be, I could not detect the other hydrogen lines.

To put a *saline solution* into an electric spark or discharge, I took a clear glass tube, open at both ends, 10 c.m. long by 3 c.m. diameter, fitted with glass taps in the sides, towards the top and bottom, to admit a current of pure air or hydrogen. In the lower end of the tube I fitted a plug of pure rubber, very slightly tapered, pierced by a platinum rod 3 m.m. diameter, terminating above in a tripod of the same metal, and having a hole below to make contact with the positive electrode.

I placed on the tripod a platinum dish slightly smaller than the diameter of the tube, containing a hollowed cone of this metal with a capillary hole through it, the top of which was about 2 m.m. above the top of the dish. I filled this dish with the saline solution to be put in a spark or discharge which flashed from the liquid covering the top of the cone.

The upper end of the tube was fitted with a slightly tapered plug of *pure* rubber, pierced by a pure platinum rod 3 m.m. diameter, terminating below in a point, and with a hole above to make contact with the negative electrode.

Before receiving the saline solution to be put into the electric spark or discharge, the dish as well as the platinum cone held in it were washed with very dilute hydrochloric acid, then with pure water, and finally made white-hot.

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* Chemical News, vol. lxxii., p. 226 (2nd footnote).

The terminal point of the platinum rod, before being adjusted vertically above, and from 2 to 3 m.m. from the top of the platinum cone, was treated in the same way as the dish.

Thanks to the pure rubber plug, this apparatus preserved perfectly the pure air and hydrogen contained in it. When working in air, the liquid, being in contact with platinum *only*, yielded, on spectrum analysis of the spark saturated with the liquid which rose by capillarity to the top of the cone, the spectrum proper to the compound, to which nevertheless was often added the red hydrogen line. Spectrum analysis of a spark showed the same spectrum, to which was added some atmospheric lines. When passing a spark or discharge in hydrogen, one saw the spectrum of the saline liquid, to which was added either the red hydrogen line or the reddish and the bluish green, or more frequently greenish blue, hydrogen lines.

When one substitutes, as is generally done, for the apparatus arranged as described above, a glass tube which is itself used to hold the saline solution, and when one prolongs for some time the sparks, and, better still, the discharge, one notices that the spectrum seen shows the sodium D line and some calcium lines, even though the saline solution in the tube contains *neither sodium nor calcium.* As a matter of fact, in the apparatus usually used, the calcium and sodium are obtained from the glass by the attack on the tubes near the platinum wires, and especially on the small glass cone, which admits the wire used for the positive electrode.

When using apparatus of which all parts to be put in contact with a saline solution are made of platinum, the method of analysing a spark or discharge saturated with a saline solution shows an advantage over the analysis of a spark or discharge passed between balls or cones coated with solid compounds, whether anhydrous or hydrated. In fact, in the former apparatus, one can make the compounds with which one wishes to saturate the spark or discharge, in a close tube filled with air or hydrogen. Relying on this possibility I tried to ascertain whether one could get, by means of calcium oxide, hydrochloric acid, or nitric acid, *free from sodium*, some dissolved chloride or nitrate of calcium, which, when introduced into a spark or discharge, would not show the sodium line on spectrum analysis, a thing I could not accomplish with compounds made in the open air. I showed this possibility, and I satisfied myself *absolutely* that the presence of sodium in a chloride or nitrate prepared in the open air is due to the sodium contained in the air. In the notes on the flame and electric spectra of chloride and nitrate of calcium I describe my observations on this point.

The method of experimenting described above has a fault which I ought to mention. It is, in many instances, a fact that spectrum analysis of a spark or discharge, in a strong or weak, neutral or acid, solution of any of the metallic compounds, fails to show always a spectrum containing *all the characteristic lines of these compounds.*

In many cases the spectrum is incomplete. Thus, whatever spectroscope be used, spectrum analysis of a spark through a sodium salt only shows *one-third* of the lines seen in the electric spectrum of sodium salts.

Experience has taught me that the greater or less volatility of the compounds is not the reason of the appearance of complete or incomplete spectra; for a spark, which only shows one-third of the lines in the electric spectrum of sodium, shows a barium spectrum identical with that of an electric arc saturated with barium.

According to my experience and the checks to which I have submitted my researches, in collaboration with M. Depaire, this method of spectroscopic research, whatever services it may have yielded, is not competent to give a decisive indication as to the *presence* or *absence* of a given body in a compound submitted to analysis.

E. *On the Holders used to Volatilise Different Bodies in an Electric Arc.*—To volatilise the different bodies in which I was carrying on my investigations in an electric arc, I first acted in the same way as when placing the same bodies in an electric spark or discharge,—that is to say, I used rods of pure carbon, of considerable length and diameter, with their extreme ends covered with these bodies, just as I have already described in notes on my studies of different metals and metallic compounds. But I soon learnt the weak points, or I might even say the errors of principle, which are associated with this method of experimenting. The voltaic current being established by connecting the poles and the volatilising of the compounds which covered them, the poles were brought at once to the brightest incandescence. This incandescence was less or greater according as the electrodes were in contact or were separated to make an electric arc. The sum of the light from the poles and from the electric arc proper are said to form *the electric light.*

But in his researches "On the Temperature of the Carbon Poles at the Instant they make the Electric Light, and on the Temperature of the Electric Arc,"* Rossetti found, at the end of the *positive* pole, a maximum temperature of 3900°, at the end of the *negative* pole a temperature of about 3150°, and in the arc itself a temperature of 4800°, whatever might be the diameter of the arc and the intensity of the current which produced it.

Besides, when looking closely into an arc which passes between two poles, one sees at once that its structure is not simple. At the beginning—that is to say, in the *crater* whence the arc springs—it emits sky-blue rays. The arc proper is of a purplish blue colour. This difference of colour between the arc at its origin and the body of it shows it to be surrounded by a pink-red gaseous envelope, of which the colour deepens gradually from the outside of the arc towards the *sky-blue* part.

The arc, at its origin, appears to me to consist of carbon *vapour*, whilst the centre is composed of the same current of carbon vapour, but partially oxidised by its contact with the air which flows continually round the arc. The colour of the envelope of the arc closely resembles the tint which the inner cone of an oxyhydrogen blowpipe assumes when one puts a filament of pure carbon into it. Since an oxyhydrogen blowpipe supplies a considerable excess of hydrogen mingled with oxygen, the carbon burns in it with the greatest brilliancy, and the flame produced thus is either red or pink, according as one looks at it near the point where the filament is held in the blowpipe, or at a part distant from that point. I have seen the same pink-red colour when distilling silver contained in a pure carbon retort in an oxyhydrogen or oxy-coal-gas blowpipe. The flame which issues from the retort is pink-red, in spite of the large quantity of silver vapour it contains.

The temperature of the gaseous envelope surrounding the arc is excessive. It greatly exceeds the fusing-point of pure platinum, which is that of the inner cone of an oxyhydrogen flame. In fact, pure iridium attached to a carbon filament melts rapidly when put into it.

Pure iridium which one drops into the *crater* of an arc *two and a half c.m.* long, with a carbon spatula, is volatilised at once, and in a very short time covers the negative pole with small drops of melted iridium.

The poles emit *heat* rays; the arc emits both *electric* and *heat* rays; as determined in my researches on the heat and electric spectra of sodium in an electric arc. When one projects into the slit of a spectroscope, a beam of parallel rays from the poles and the arc at once, and saturates the arc with a volatilised compound which has a *different* heat and electric spectrum, the image has the characteristic lines of both spectra.

It follows from these facts that, when using an electric arc to study the spectrum of a body, one ought to throw parallel rays coming from the poles, and parallel rays coming from the arc, *separately* on the slit of the spectro-

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* *Annales de Chimie et de Physique*, Fifth Series, vol. xviii.. p. 476 Paris, 1879.

scope, as I have taken care to do since I have understood the complexity of the electric light.

(To be continued).

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.[*]

By C. E. LINEBARGER.

(Continued from p. 239).

Vapour-tensions of Mixtures of Acetic Acid with Benzene and with Toluene.

Two series of determinations were carried out on the mixtures of benzene and acetic acid, one at 35° and one at 20°, but one, however, for the mixtures of toluene and acetic acid, at 35°. In order to apply to the experimental results of the work our mode of calculation of the vapour-tensions, it is necessary to know the molecular mass of gaseous acetic acid at the above two temperatures. Now acetic acid even in the vapourous condition is made up in part of polymerised molecules, so that it is not legitimate to set its molecular mass equal to that corresponding to the formula $C_2H_4O_2$. What the actual molecular mass of the gaseous acid at 35° and 20° is can be easily calculated by the aid of the vapour-density determinations of Bineau ("Recherches sur les Relations des Densités des Vapeur avec les Equivalents Chimiques;" *Ann. Chim. Phys.*, xviii., 226, 1846), which are the more applicable to the case in hand as his vapour-density measurements were made under the same conditions as my vapour-tension determinations; that is to say, Bineau measured the amount of acetic acid that diffused into a definite volume of air at a fixed temperature. The molecular mass of acetic acid as deduced from Bineau's observations is 104 for 35° and 110 for 20°. It may be worth while to remark that an error of five in the molecular mass will not entail an error of 1 millimetre in the vapour-tension; we may with all confidence then adopt the above molecular masses of acetic acid in state of vapour as quite accurate.

The necessary data of the experiments are given in Tables X. to XII.; the superscription to each vertical column renders any explanation of them here superfluous.

TABLE X.—*Vapour-Tensions of Mixtures of Benzene and Acetic Acid at 35°.*
Vapour-tension of Benzene at 35° is 146 m.m. of Mercury.
Vapour-tension of Acetic Acid at 35° is 26·5 m.m. of Mercury.

P.c. of $C_2H_4O_2$ in liquid mixt.	P.c. of $C_2H_4O_2$ in gaseous mixt.	Grms. $C_2H_4O_2$ in vapour.	Grms. C_6H_6 in vapour.	Tension of $C_2H_4O_2$ in m.m.	Tension of C_6H_8 in m.m.	Volume of air in m.m.	Barometer in m.m.	Internal pres. m.m.
6·44	2·45	0·0461	1·3759	3·5	140·0	1955	758	14
15·17	4·74	0·0834	1·3580	6·4	129·2	1958	758	15
37·10	8·25	0·0700	1·5840	10·5	117·0	1020	767	16
43·99	11·02	0·0867	0·5243	13·2	106·5	1019	766	16
49·86	12·26	0·0931	0·4849	14·0	103·1	1020	766	17
53·24	13·33	0·0969	0·4731	14·9	97·6	1020	766	17
54·65	13·82	0·0990	0·4630	15·3	97·3	1020	766	17
56·60	14·62	0·1063	0·4677	16·4	96·0	1020	766	17
73·87	20·18	0·1156	0·4585	18·4	72·7	1019	766	16
80·00	26·91	0·1351	0·2751	22·3	59·3	1020	766	17

TABLE XI.—*Vapour-Tensions of Mixtures of Benzene and Acetic Acid at 20°.*
Vapour-tension of Benzene at 20° is 75·6 m.m. of Mercury.
Vapour-tension of Acetic Acid at 20° is 11·7 m.m. of Mercury.

P.c. of $C_2H_4O_2$ in liquid mixt.	P.c. of $C_2H_4O_2$ in gaseous mixt.	Grms. $C_2H_4O_2$ in vapour.	Grms. C_6H_6 in vapour.	Tension of $C_2H_4O_2$ in m.m.	Tension of C_6H_6 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pres. m.m.
53·24	11·99	0·0440	0·2291	6·6	48·7	1018	760	16
80·00	21·97	0·0576	0·2100	9·1	33·0	1018	760	16
97·28	64·66	0·0674	0·0276	11·4	6·2	1018	760	16

TABLE XII.—*Vapour-Tensions of Mixtures of Toluene and Acetic Acid at 35°.*
Vapour-tension of Toluene at 35° is 47·2 m.m. of Mercury.
Vapour-tension of Acetic Acid at 35° is 26·5 m.m. of Mercury.

P.c. of $C_2H_4O_2$ in liquid mixt.	P.c. of $C_4H_4O_2$ in gaseous mixt.	Grms. $C_2H_4O_2$ in vapour.	Grms. C_7H_8 in vapour.	Tension of $C_2H_4O_2$ in m.m.	Tension of C_7H_8 in m m.	Volume of air in c.c.	Barometer in m.m.	Internal pres. m.m.
49·00	32·66	0·0911	0·1661	15·0	31·8	1020	760	18
60·88	37·91	0·1025	0·1485	17·4	28·5	1020	760	18
83·37	56·36	0·1252	0·0858	22·2	16·7	1020	760	18

TABLE XIII.—*Partial Pressures of Benzene, Acctie Acid, and Toluene.*

Per cent of $C_2H_4O_2$ in liquid mixture.	Partial pressure of C_6H_6 at 35° in m.m.	Partial pressure of $C_2H_4O_2$ at 35° in m.m.	Partial pressure of C_7H_8 at 35° in m.m.	Partial pressure of C_6H_6 at 20° in m m.	Partial pressure of $C_2H_4O_2$ at 20° in m.m.
10	138·4	2·8	44·5	71·4	1·2
20	130·9	5·6	41·6	67·5	2·3
30	122·2	8·2	38·6	63·1	3·5
40	112·6	11·1	35·0	58·2	4·8
50	102·4	13·6	31·9	53·2	6·0
60	90·7	16·2	27·8	47·1	7·2
70	76·7	19·1	23·1	40·1	8·4
80	59·1	21·7	18·4	31·1	9·6
90	35·1	24·2	11·1	18·5	10·7

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[*] Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

From these data curves were constructed on a large scale with percentages of composition as abscissæ and vapour-tensions as ordinates (1 inch on the axis of abscissæ corresponded to 5 per cent; 1 inch on axis of ordinates to 10 m.m. of pressure); these proved to be perfectly regular, and passed directly through most of the points.

The points for acetic acid either fell upon or very close to the straight line connecting the left hand origin of the co-ordinate system with the point on the right hand axis of ordinates corresponding to the value of the vapour-tension of pure acetic acid at the temperature in question, viz., 26·5 for 35°, and 11·7 for 20°, the acetic acid vapour-tension curve is simply a straight line, then, when the composition is expressed in percentages. An interesting conclusion to be drawn from this fact is that the partial tension of acetic acid is the same, be it mixed with benzene or with toluene; the specific influence of the diluting liquid seems to be extremely slight, if, indeed, there is any at all. This circumstance also indicates that the molecular condition of the acid is the same when it is dissolved in either of the hydrocarbons so as to form solutions of the same strength; this insight into the molecular structure of acetic acid enables us to determine by a little calculation its molecular mass not only in the dissolved but also in the pure state. In the following section will be set forth the *modus operandi*.

From the curves drawn as just described above, the partial pressures of the various constituents of the mixtures were taken for concentrations corresponding to 10, 20, 30, ... 90 per cent of acetic acid; the data thus obtained are given in Table XIII.

(To be continued)

THE QUANTITATIVE DETERMINATION OF PERCHLORATES.*

By D. ALBERT KREIDER.

(Continued from p. 242).

The results obtained by substituting (*a*) cadmium iodide and (*b*) anhydrous zinc chloride for the double chloride of aluminum and sodium are recorded in Table VI. In (27), (28) and (29) cadmium iodide was used, and the iodine obtained by treating the cooled mass with dilute sulphuric acid (1 : 6) and potassium iodide for the reduction of cadmium oxide in each case added to that of the receivers. In (30) and (31) zinc chloride was employed, but no additional iodine was obtained by treatment with sulphuric acid and potassium iodide.

Table VI.

	$KClO_4$ taken. Grm.	$KClO_4$ found. Grm.	Error. Grm.
(27)	0·1000	0·0745	0·0255 −
(28)	0·1000	0·0693	0·0307 −
(29)	0·1000	0·0679	0·0321 −
(30)	0·1000	0·0245	0·0755 −
(31)	0·1653	0·1156	0·0497 −

In (31) manganous chloride was mixed with the zinc chloride in the proportion of 2 : 1, in the hope of strengthening the reducing action. The black colour of the fusion revealed the formation of manganese dioxide, the equivalent of which in iodine was obtained by dissolving the cooled mass in water, adding dilute sulphuric acid and a known amount of ammonium oxalate, titrating the residual oxalate with permanganate solution, and calculating the difference into iodine, which was added to that obtained by titrating the contents of the receivers. This addition of manganous chloride to the fusion of the double chloride of aluminum and sodium was forestalled by the necessity of subsequent solution of the fused mass, which contained an impurity in the form of ferric chloride, which of course in the presence of hydriodic acid would be reduced with evolution of iodine.

It was evident from all these results, as well as those obtained by use of other salts not necessary here to record, that fusion with salts of the halogens would not suffice for the complete reduction of perchlorates, or at least would not quantitatively register the result in the halogen liberated. The well-known reaction of the oxidation of chromic oxide by fusion with alkaline carbonates was also applied. A combustion-tube was used for the fusion, sealed at one end, and, after the insertion of chromic oxide with a mixture of sodium and potassium carbonate, restricted at the other end so as to admit a small tube by which carbon dioxide could be entered to expel all air. A blank determination gave no chromate. When 0·1 grm. potassium perchlorate was mixed with an excess of chromic oxide and alkaline carbonate, and carefully fused from the top, and kept in a state of fusion throughout its length in an atmosphere of carbon dioxide, the fusion subsequently dissolved in water, and the chromic oxide removed by filtration, an amount of chromate was obtained on titration equivalent to only 0·0347 grm. of potassium perchlorate.

Powerful as were the various reducing agents employed for the decomposition of perchlorates, they were all successfully resisted, even at the highest permissible temperatures; and if anything is proved by the results of the experiments above recorded, it is that perchloric acid is, in combination, one of the most powerful and stable acids known. Certainly nothing short of high temperatures is capable of overcoming the remarkable affinity by which the oxygen of this acid is held by its salts. At about 400° C. the potassium salt fuses with evolution of oxygen, and as a last resort an attempt was made to have the oxygen thus obtained act on hydriodic acid by intervention of nitric oxide. It was the application of this principle that led to the final method, which, both as to manipulation and results, leaves nothing to be desired.

The method is essentially the collection of the oxygen of the perchlorate; its subsequent passage into an atmosphere of nitric oxide over a strong solution of hydriodic acid, and the titration of the iodine thus liberated with decinormal arsenic in alkaline solution. The apparatus employed consisted of a piece of combustion tubing 10 or 12 c.m. in length, drawn out at one end to a narrow restriction of length sufficient to prevent the action of the heat on the rubber tubing connecting it with a receiver filled with caustic potash. The tube must of course be cleansed from all organic materials, and cannot be safely employed for more than three fusions. A platinum boat (porcelain fusing to the glass) served for the introduction of the perchlorate to the combustion-tube, and, in order to bring about a gradual and quiet fusion, the perchlorate was covered with a small amount of an equal mixture of dry and pure sodium and potassium carbonates. Carbon dioxide obtained from a Kipp generator, the acid and marble of which had been previously boiled to expel all traces of air, and to which a little cuprous chloride had been added to take up any oxygen which might be absorbed from the top, was passed through a solution of iodine in potassium iodide to remove a trace of reducing agent which it was found to contain, and then washed with potassium iodide solution before being used. The larger end of the combustion-tube was closed with a perforated rubber stopper by which it was attached to the carbon dioxide apparatus. After all air had been expelled from the inclined tube by means of carbon dioxide, it was connected by a short glass capillary and vacuum tubing joints with the receiver, into which about 50 to 100 c.m.^{3} of gas was allowed to flow before the combustion was started, and thus, when only a small but inevitable bubble remained insoluble in the caustic potash, the complete removal of air was indicated. To prevent the caustic potash from drawing into the combustion-tube, a little

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* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. l., October, 1895.

more carbon dioxide was entered, when the current was closed by a pinchcock on the side towards the generator, and heat gradually applied—with perforated asbestos cards on either side to check its radiation to the rubber—and continued till the contents of the platinum boat was in a quiet state of fusion. By lowering one of the bulbs of the caustic potash receiver, the oxygen was evolved under slightly diminished pressure, and thus the chances of loss decreased. Then the tube was again inclined and carefully annealed, while a current of carbon dioxide carried all of the oxygen into the receiver, which was then closed and disconnected. As a receiver, two levelling bottles were found vastly superior to a burette, the glass stopcocks of the latter giving continual trouble by the action of the caustic potash upon them. I found that gas could be removed from a levelling bottle without the loss of a particle, if a perforated rubber stopper containing a capillary tube, which reached just even with the narrower end, was by a slight twist forced tightly into the neck of the bottle. In this way a regular funnel-shape was obtained, and the oxygen could be withdrawn without the slightest bubble remaining. The other end of the capillary was fitted with a short piece of vacuum tubing and screw pinchcock, which worked incomparably better than the glass stopcocks. The larger capacity of the bottle was favourable for the volume of oxygen evolved, and its shape offered superior facilities for the absorption of carbon dioxide.

For the action of the oxygen on hydriodic acid through the medium of nitric oxide, various devices were tested. Passing it directly into nitric oxide over a solution of hydriodic acid in a Hempel absorption bulb was found to yield low and irregular results, due doubtless to the formation of nitric acid wherever the nitrogen trioxide or peroxide, as the case might be, met water in which the hydriodic acid had been exhausted,—as, for instance, along the sides of the bulb. Shaking the bulb as the oxygen entered improved the action, but was not sufficient. It was evident that, for a complete action, the hydriodic acid solution must be strong and on the spot where the higher oxide of nitrogen is formed; and to avoid excessive use of the iodide the volume of water must be kept at a minimum. Letting a solution of hydriodic acid saturated with nitric oxide flow slowly into the Hempel bulb in which the oxygen was contained over water, was so slow in its action that a quantitative test was not applied. The plan of mixing the two gases under a strong solution of hydriodic acid by means of two capillaries with adjoining openings, was more effective and rapid, but it was wasteful of nitric oxide, which for complete action would have to flow in continual excess, whereas only a small amount of nitric oxide would really be necessary for the reaction, since it could be used and re-used for the transfer of free oxygen to the hydriodic acid. A simple piece of apparatus was then devised to meet all these conditions. It consisted of a 100 c.m.³ bulb pipette, cut off short at either ends with stopcocks sealed to both stubs. The delivery-tube of one of the stopcocks was cut off rather short after being tapered and restricted so as to hold a rubber connecter tightly, while the other delivery-tube was left long enough to reach to the bottom of an Erlenmeyer beaker. It is a convenience to have these conducting tubes 3 or 4 m.m. in diameter rather than capillaries, since for the various connections all air may be expelled from them by displacement with water, which is easily accomplished by using a long-nozzled wash-bottle. By attaching the shorter end to an ordinary water-pump the air was partially exhausted, when the stopcock was closed, and the bulb disconnected and lowered into a solution of hydriodic acid of approximately known strength, obtained by acidifying potassium iodide with hydrochloric acid. When the desired amount of liquid had been drawn in, the stopcock was closed and connection made with the carbon dioxide, by which all residual air was expelled. Then the bulb, held so as to prevent the escape of the liquid, was again exhausted by attachment to the pump. After about 10 c.m.³ of nitric oxide were admitted, attachment was made to the receiver containing the oxygen, which was allowed to enter slowly under the diminished pressure within the bulb, and with continuous shaking of the contents of the latter. The latter precaution is essential to the process, as otherwise there is imperfect distribution of the hydriodic acid and the danger of forming nitric acid. But when the solution of hydriodic acid is kept strong, and the shaking continued while the oxygen enters and for a minute or two afterward, depending on the rapidity with which it was admitted, the oxygen may be allowed to enter quite rapidly without any fear of imperfect action. The oxygen being immediately utilised, the partial vacuum is effected only by the heat generated, which is scarcely noticeable. As a rule, the bulb and contents were well cooled before the oxygen was admitted.

(To be continued).

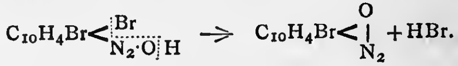
PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

The following are the abstracts of papers received during the vacation, and published in the *Transactions*:—

104. "*Homonucleal Tri-derivatives of Naphthalene.*" By Raphael Meldola, F.R.S., and Frederick William Streatfeild.

Dibromonitronaphthalene, $C_{10}H_5Br{\cdot}NO_2{\cdot}Br$ (1 : 2 : 4), m. p. 117°, has been prepared by the authors and submitted to further study. The corresponding dibromo-β-naphthylamine consists of white silky needles melting at 106—107°; the acetyl-derivative melts at 220—221°. When this dibromo-β-naphthylamine is diazotised in the presence of an excess of mineral acid and the diazo-salt solution boiled with water, the NH_2-group is not replaced by hydroxyl, as in the normal Griess reaction, but bromine is displaced, and a diazoxide formed in accordance with the scheme—



$$C_{10}H_4Br<\begin{matrix}Br\\N_2{\cdot}O\,H\end{matrix} \rightarrow C_{10}H_4Br<\begin{matrix}O\\|\\N_2\end{matrix} + HBr.$$

The diazoxide has the constitution $\overline{O : N_2} : Br = 1 : 2 : 4$. It consists of ochreous needles, soluble in boiling water, and decomposing at 148—151°. It is reduced by tin and hydrochloric acid to β-amido-α-naphthol, and bromine and glacial acetic acid converts it into dibromo-α-naphthaquinone, m. p. 216°.

Chlorobromo-β-naphthylamine, $C_{10}H_5Cl{\cdot}NH_2{\cdot}Br$ (1 : 2 : 4), was obtained in the form of white silky needles melting at 102—103°; the acetyl derivative at 218°, the benzoyl derivative at 185—186°. By nitrous acid this chlorobromo-β-naphthylamine is converted into the diazoxide, above described, in the presence of excess of mineral acid; in its absence the diazoamide, $C_{10}H_5ClBr{\cdot}N_2{\cdot}NH{\cdot}C_{10}H_5ClBr$, is formed. This compound is very stable for a diazoamido-compound, and crystallises from toluene in yellowish needles melting at 205—210°, with decomposition. The authors also show that iodine chloride is an excellent reagent for preparing iodine derivatives of the acetnaphthalides, both α and β. They give the melting-points of the following compounds:—$C_{10}H_4I{\cdot}NHAc$ (4 : 1), 197°; $C_{10}H_5{\cdot}NO_2{\cdot}I{\cdot}NHAc$ (2 : 4 : 1); $C_{10}H_5{\cdot}NO_2{\cdot}I{\cdot}OH$ (2 : 4 : 1), 150° (shrinking at 147°); $C_{10}H_5{\cdot}NO_2{\cdot}I{\cdot}OC_2H_5$ (2 : 4), 104—105°. The potassium salt of the nitroiodonaphthol has also been prepared and analysed.

105. "*The Ethereal Salts of the Optically Active Lactic Chloropropionic, and Bromopropionic Acids.*" By J. Wallace Walker, M.A.

The methylic, ethylic, and propylic ethereal salts of active lactic acid were prepared by the action of the alkyl iodides on the anhydrous silver salt. From the ethereal lactates the corresponding bromopropionic salts were prepared by the action of phosphorus pentabromide. For both series of salts there is a constant difference in rotatory power, in the first case of 5·5°, in the second of 14·2°, between two adjacent members. The ethereal chloropropionates were prepared by the action of phosphorus pentachloride on lactic acid. These bodies possess a high degree of optical activity, and the values given in this paper are much higher than those found by Le Bel, Walden, and Frankland and Henderson for such of the substances as they have examined. The observed results do not agree with Guye's hypothesis.

106. "*Some New Azo-compounds.*" By Charles Mills.

By the action of nitrosobenzene on aniline dissolved in acetic acid azobenzene is produced (Baeyer, *Ber.*, vii., 1638). The author has extended this reaction, and has prepared the following substances:—

m-*Acetylamidoazobenzene*, m. p. 130—131° C. On hydrolysis with caustic soda it gives m-*amidoazobenzene*, crystallising from light petroleum spirit in long, silky, orange needles, m. p. 56—57° C. Readily soluble in alcohol, acetic acid, ethyl acetate, acetone, chloroform, benzene, and ether. $C_6H_5{\cdot}N_2{\cdot}C_6{\cdot}H_4{\cdot}N_2{\cdot}C_6H_5$, *diparadiphenyldisazophenylene*, prepared by the action of nitrosobenzene on *p*-amidoazobenzene. p-*Benzeneazotoluene* formed by the action of nitrosobenzene on *p*-toluidine, also by the action of *p* nitrosotoluene on aniline.

The following compounds are also described:—

p-*Benzeneazotoluenesulphonic Chloride*. p-*Benzeneazo*-o *acettoluide*, $C_6H_3{\cdot}CH_3{\cdot}NHAc{\cdot}N{:}N{\cdot}C_6H_5$ (1 : 2 : 4). m-*Amido* p-*benzeneazotoluene*. *Benzene*-o-*azo*-o-*acettoluide*, $C_6H_4{\cdot}NHAc,CH_3{\cdot}N{:}N{\cdot}C_6H_5$ (1 : 2 : 3). m-*Amidobenzene*-o-*azotoluene*, $C_6H_4{\cdot}NH_2{\cdot}CH_3{\cdot}N_2{\cdot}C_6H_5$ (1 : 2 : 3).

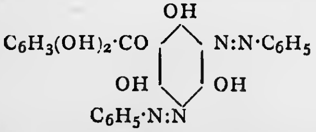
107. "*Some Derivatives of Maclurin.*" By C. S. Bedford and A. G. Perkin.

When an aqueous extract of old fustic (*Morus tinctoria*(is treated with a solution of diazobenzene sulphate, a colouring-matter is produced. The chief constituents of old fustic are, morin, $C_{15}H_{10}O_7$, and maclurin, $C_{13}H_{10}O_6$, only the latter reacts readily with diazobenzene. Benzeneazomaclurin,—

$$C_{13}H_8O_6(C_6H_5{\cdot}N_2)_2,$$

o- and *p*-tolueneazomaclurin, *p*-nitrobenzeneazomaclurin, and maclurinazobenzene-*p*-sulphonate of sodium have also been prepared. These substances dye wool and silk orange-coloured to deep brown shades. Maclurin, by the action of reducing agents, yields phloroglucin and protocatechuic acid, and is considered to be a pentahydroxybenzophenone, $C_6H_3(OH)_2{\cdot}CO{\cdot}C_6H_2{\cdot}(OH)_3$.

Phloroglucin combines with 2 mol. props. of diazobenzene, while no reaction takes place between this latter and protocatechuic acid. The constitution of benzeneazomaclurin should therefore be thus represented,—



108. "*The Constituents of 'Artocarpus integrifolia.'*" By A. G. Perkin and F. Cope.

Artocarpus integrifolia is the well-known Jack Fruit, cultivated in India, Burmah, and Ceylon. It is much esteemed for carpentry, and is used in conjunction with alum as a yellow dye. It contains a yellow colouring matter of the formula $C_{15}H_{10}O_7$, identical with *morin*, and a substance of the formula $C_{15}H_{12}O_6$, to which the name *cyanomaclurin* has been given. With diazobenzene it yields a compound, $C_{15}H_{10}O_6(C_6H_5N_2)_2$, crystallising in scarlet needles, which dyes unmordanted wool and silk orange to orange-red shades, but which does not dye with mordants. When boiled with dilute acids, cyanomaclurin yields red-brown products, resembling in character the so-called "anhydrides" of catechin, which can be produced from this latter substance in a similar way. That first formed dissolves in hot water and dilute alkalis, but by longer treatment becomes more sparingly soluble, and the final product obtained is insoluble in dilute alkalis and the usual solvents. No glucose is produced during this reaction, so that cyanomaclurin is not a glucoside. The study of this substance will be continued.

109. "*Optically Active Methoxy- and Propoxy-succinic Acids.*" By T. Purdie, F.R.S., and H. W. Bolam, B.Sc.

The authors have resolved inactive methoxy- and propoxy-succinic acids into their active components, the cinchonine and strychnine salts being made use of in the case of methoxysuccinic acid, the strychnine salts in the case of the propoxysuccinic acid.

Rotations of the acids in water and different organic solvents are given, with the rotations of salts of both acids in aqueous solution.

110. "*Ethereal Salts of Active Methoxy- and Ethoxy-Succinic Acids.*" By T. Purdie, F.R.S., and S. Williamson, Ph.D.

Inactive methoxy- and ethoxy-succinic acids were resolved into their active components by means of their strychnine salts. Observations on the activity of the various strychnine salts in aqueous solution were made, and results obtained in accordance with the law of Oudemans.

Methyl-, ethyl-, propyl-, and butyl-, methoxy-, and ethoxy-succinates, and the isopropyl and isobutyl salts of ethoxysuccinic acid, were prepared by the action of their respective iodides upon the silver salts of the acids, and their rotations observed.

The specific rotations of the active acids in water and various organic solvents were also taken. A discussion of the results obtained is contained in the paper.

111. "*Note on the Production of Potassium Platinichloride.*" By E. Sonstadt.

Dry potassium platinichloride, when heated with mercury, is decomposed according to the proportion of mercury used.

(1). $2KCl,PtCl_4+4Hg=2KCl+Pt+4HgCl.$
(2). $2KCl,PtCl_4+2Hg=2KCl+Pt+2HgCl_2.$

The decomposition begins even below 100° C., and is complete at a lower temperature than is required to expel from the containing vessel the mercurous or mercuric chloride produced.

In treating small quantities of the platinichloride, the mercury is placed in a porcelain crucible, and covered with platinichloride, in the proportion of about two parts of mercury to one of salt. Heat is applied very gently, to avoid loss through boiling, till the reaction is complete, when the heat is raised to expel the mercurous chloride.

When larger quantities are decomposed, the salt is preferably triturated with the mercury, and gently heated, so as to avoid a too sudden or violent reaction.

Additional Note by Author.—Dry silver chloride is not decomposed by mercury, even at a red heat; nor when mixed or combined with a platinum salt.

112. "*Orthobenzoic Sulphinide.*" By William J. Pope.

The author finds that pure orthobenzoic sulphinide in large well-defined crystals may be obtained from the commercial mixture known as "saccharin," by crystallisation from acetone. Crystallographical measurements are given.

113. "*Derivatives of β-Resorcylic Acid.*" By A. G. Perkin.

The principal product of the action of methylic iodide upon β-resorcylic acid is a substance crystallising in needles melting at 76—77°, and having the constitution $C_6H_2{\cdot}Me(OMe){\cdot}OH{\cdot}COOMe$. It appears probable that the hydroxyl group in β-resorcylic acid, which resists methylation, is in the *o*-position to the carboxyl group.

The principal product of the action of ethylic iodide upon β-resorcylic acid is insoluble in alkalis, and contains but two ethoxy groups. It has the formula—

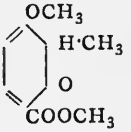
$$C_6H_3(OEt)(OH)\cdot COOEt.$$

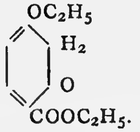
The action of methylic iodide upon resacetophenone has been studied, but the results have been anticipated by Gregor (*Monatsh.*, 1894, xv., 437). The principal product is a substance having the constitution—

$$C_6H_2(OMe)\cdot Me\cdot(OH)\cdot COCH_3,$$

insoluble in alkalis, and resembling the results of the action of methylic iodide upon β-resorcylic acid.

It appears probable that the insolubility of the methyl and ethyl ethers of β-resorcylic acid and resacetophenone, which apparently contain a free hydroxyl group, is due to the fact that the oxygen of this latter has assumed the ketonic form. The constitution of the two former substances would therefore be—





Preliminary experiments on the methylation of gallacetophenone have yielded a substance melting at 76—77°, apparently a dimethyl ether, $C_6H_2(OMe)_2\cdot OH\cdot CO\cdot CH_3$.

Gallacetophenone oxime, $C_6H_2(OH)_3\cdot C:NOH\cdot CH_3$, and *quinacetophenone oxime*, $C_6H_3(OH)_2\cdot C:NOH\cdot CH_3$, were also obtained.

114. "*Note on the Gravimetric Estimation of Maltose by Fehling's Solution.*" By T. A. Glendinning.

The specific cupric-reducing power of maltose possesses a different value according to whether potash or soda is the alkali employed in the preparation of Fehling's solution. Under the conditions of experiment given, the reducing powers to be attributed to maltose are—

Soda, $K_{3.86}=61$. Potash, $K_{3.86}=64$.

On making comparative analyses of starch-transformation products with the two kinds of Fehling's solution, identical results were obtained, provided the respective values of K were used.

No such difference occurs in the case of dextrose or of invert sugar.

115. "*Studies in the Malonic Acid Series.*" By S. Ruhemann, Ph.D., M.A., and K. J. P. Orton, B.A.

The authors have investigated the action of ammonia, hydrazine, and phenylhydrazine on dibromomalonamide. Ammonia yields diaminomalonamide, $C(NH_2)_2(CONH_2)_2$; and hydrazine and phenylhydrazine give the hydrazone and phenylhydrazone respectively of malonamide.

Fuming nitric acid acts on malonamide, forming nitromalonamide. Aniline, when heated with nitromalonamide until ammonia ceases to come off, yields diphenylurea.

On reduction of nitromalonamide with sodium amalgam, aminomalonic acid is obtained.

By permission of Professor Claisen, the authors have investigated the action of hydrazine hydrate on ethyl ethoxymethylenemalonate. They obtain a result which does not agreee with that of V. Rothenberg.

116. "*Mercury Perchlorates.*" By M. Chikashigé.

Mercuric perchlorate is not anhydrous, its composition being $Hg(ClO_4)_2,6H_2O$. It slowly loses, in a desiccator, acid and water, and effloresces. In the air it is very deliquescent (Serullas). When heated, it melts completely at 34° (in dry air); as the temperature rises to 150°, it very slowly decomposes, giving off water and perchloric acid, while a white basic perchlorate, $Hg_3O_2(ClO_4)_2$, is left, permanent at that temperature. If the salt is heated in a long narrow tube, it may be kept in a bath at 400° for any time, without permanent decomposition, boiling freely and retaining its transparency, and, when cooled, solidifying unchanged. Whilst heated it is, however, continuously decomposing into basic salt and acid and water; but as the acid and water vapours condense and flow back, the salt is continuously re-formed, and presents only the phenomena of ebullltion.

Mercurous perchlorate has the composition—

$$(HgClO_4)_2,4H_2O,$$

according to the author; Roscoe found $6H_2O$. In a vacuum desiccator it loses in two weeks $2H_2O$ and a very little acid, and then ceases to lose weight. It is slowly decomposed by heat, even at 100° or less, in dry air, first losing water and perchloric acid; then gradually, from 150° upwards, becoming mercuric salt, and yielding chlorides and a little chlorate. It resembles mercuric perchlorate in its decomposition, but does not show the phenomena of fusion and ebullition. According to Roscoe, mercurous perchlorate does not lose weight in a vacuum over sulphuric acid, or at 100°.

117. "*a-Ethylene Dihydroxylamine Dihydrobromide.*" By C. M. Luxmoore, D.Sc.

When ethylene bromide is heated with a solution of hydroxylamine in methyl alcohol to 100°, two mols. of the latter combine with one of the former to form the dihydrobromide of ethylene dihydroxylamine, a white crystalline substance, soluble in water and alcohol, insoluble in ether. When reduced with hydriodic acid, all the nitrogen is obtained as ammonia. The constitution of the substance is therefore—

$$\begin{array}{l} CH_2\cdot O\cdot NH_2\cdot HBr \\ | \\ CH_2\cdot O\cdot NH_2\cdot HBr, \end{array}$$

and its formation lends some support to the view that free hydroxylamine has the structure $O{=}NH_3$.

Ethylene oxide also reacts with hydroxylamine, forming apparently the base correponding with the hydrobromide described above.

118. "*The alleged Isomerism of Potassium Nitrososulphate.* By C. M. Luxmoore, D.Sc.

Potassium nitrososulphate, whether prepared by the absorption of nitric oxide, by potassium sulphite, or by the absorption of a mixture of sulphur dioxide and nitric oxide by potassium hydroxide, has always the same properties. Hantzsch's silver salt, $(KAgSN_2O_5)$, has been obtained from specimens prepared in these different ways, and showed the characteristic behaviour described by him.

Potassium nitrososulphate reaches a temperature of about 134° (as indicated by a thermometer embedded in the salt) before it explodes, the gradual and quiescent decomposition into potassium sulphate and nitrous oxide that precedes the explosion furnishing the heat that raises the temperature of the substance above that of the bath in which it is heated.

Pelouze's account of the properties of this substance can be completely reconciled with the recent observations of Hantzsch and of Divers and Haga, with the exception of the statement that it loses no weight when heated to 110°, which is evidently a mistake. Five minutes' heating below 105° causes a loss of weight of 2½ per cent.

There is no evidence to warrant the suggestion of Hantzch that Raschig's first salt is isomeric with potassium nitrososulphate, nor can it be regarded as identical with the salt prepared by Davy and Pelouze.

119. "*On the Freezing-points of Silver and Gold.*" By C. T. Heycock, F.R.S., and F. H. Neville.

The authors draw attention to the close agreement between the determination of the freezing-point of gold, by Callendar, in 1892, and their own determinations in 1894. The platinum temperatures differ by a few degrees, but, when reduced to the scale of the air thermometer by the same method, the two results do not differ by more than one degree. The authors further consider the influence of various gases on the freezing-point of silver. They find that the highest and steadiest freezing-points are obtained in the presence of free hydrogen or of coal-gas, and that nitrogen or carbon dioxide produce little or no depression. They find that the well-known effect of oxygen on the freezing-point of silver may amount in extreme cases to a depression of 20° C., but that the oxygen can be removed by the action of nitrogen or hydrogen.

NOTICES OF BOOKS.

The Origin and Rationale of Colliery Explosions: Founded upon an Examination of the Explosions at the Timsbury, Albion, Malago Vale, and Llanerch Collieries; and upon the principal phenomena of the Disasters at the Abercarne, Alltofts, Altham, Apedale, Blantyre, Bryn, Clifton Hall, Dinas, Elemore, Hyde, Llan, Mardy, Morfa, Mossfields, National, Penygraig, Risca, Seaham, Trimdon Grange, Tudhoe, Udstone, and West Stanley Collieries. By Donald M. D. Stuart, F.G.S., Mining and Civil Engineer, Author of "Coal-Dust an Explosive Agent." Bristol: J. Wright and Co. London: Simpkin, Marshall, and Co., Lim. New York: Hirschfeld Bros. 1895. Crown 4to., pp. 144. With two Plans.

When colliery explosions first began to attract public attention, they were considered solely due to so-called "fire-damp," *i.e.*, methane or light hydrogen carbide, which if mingled with atmospheric air forms, of course, a violently explosive total. To combat this serious evil, two distinct methods were devised. On the one hand, the ventilation of the mines was improved so that methane might be swept away as rapidly as it was generated, and might not be anywhere present in the mine in an explosive quantity. On the other hand, there was the safety-lamp in its various modifications which was to prevent any inflammable gas from being ignited by the lights used by the colliers in working. That much disaster was prevented by these two agencies is beyond all question; but still explosions occurred from time to time, though less frequently in proportion to the number of men employed underground and the weight of coal raised. To account for these calamities it was alleged that the ventilation was defective, or that the men carried down matches or picked the lock of their safety-lamps. Both these charges were doubtless true in not a few cases; but there still remained a balance of mischief not yet accounted for. It was therefore suspected—and it was ultimately demonstrated—that there must exist some other agent which might give rise to explosions, either alone or in conjunction with methane. This was found to be coal-dust, which has been studied by Prof. Galloway, and to a greater extent by the present author. Still, however, it was contended by some experts that coal-dust alone, in the total absence of methane, could not occasion an explosion. The Timsbury disaster, however, supplied the needed crucial instance. The Timsbury collieries have been worked with open lights for about seventy years, and during all the working no fire-damp has been detected. The character of the explosion, which took place in the present year, differed entirely in its features from those unquestionably due to fire-damp. In the latter, a blast seems to have swept through the workings, from end to end, occasioning wreckage everywhere. In the Timsbury disaster we have a series of eighteen distinct explosions at very considerable distances from each other. At the points of these explosions there was the usual devastation, falls of roof, shattered doors, &c., but in the intermediate spaces there was no evidence of violent forces.

A further characteristic of the two kinds of explosions appears on comparing the after-damp. Where carbonic acid is present in quantities exceeding 2·21 per cent, candles are instantly extinguished. The first physiological action encountered is difficulty of breathing, which becomes very marked if the proportion of carbon dioxide reaches 3·38 per cent. Persons who have been exposed to such an atmosphere compare its effects to those produced by violent running; whilst, according to Dr. Haldane, a proportion of 8 per cent is fatal.

The effects of "white-damp" are different; lights are not extinguished, so that the only indication of danger is the physiological action. There is felt a smarting in the eyes and nose, the legs tremble, and giddiness is experienced, and there is imminent danger unless an instant retreat into the air is practicable. In the spaces intermediate between the points of explosion some of the men were found lying dead, but not mutilated, and their lamps had not been extinguished, but in some cases had gone on burning until all their oil was consumed.

At an explosion in a similar non-fiery mine (Malago Vale colliery) "the night bailiff was found unconscious, his safety-lamp in his hand, still burning, though it had been exposed to the entire gaseous products of the explosion for nearly two hours."

The immediate cause of the explosion at the Timsbury colliery seems to have been the remarkably dry condition of the mine and the error of James Carter, who seems, in firing a "shot," to have used a much larger quantity of powder than was necessary, and to have used as tamping a mixture of coal-dust and oil. The excessive charge was partly blown out into the dry coal-dust, and set up a process of destructive distillation, liberating combustible gases. It will be perceived on inspecting the plan that the successive explosions took place where the gases met with a sufficient volume of air (*i.e.*, oxygen) to form an explosive mixture.

Mr. Stuart's recommendation for the prevention of similar catastrophes is highly judicious. He proposes that in such dry mines the coal-dust should be kept well and permanently moist; especially at the spots where a shot is to be fired the floor and the sides should be rendered quite sloppy. The evaporation of such a quantity of moisture would consume any unnecessary and dangerous heat-energy.

Concerning the proposed use of "high" explosives in place of powder for blasting, the author does not consider that our experimental knowledge is sufficient to admit of a decision.

Mr. Stuart, by the production of this unpretending work, has laid the mining interests of this country under deep obligation.

Our Chemistry of Nutrition: a Contribution to the Doctrine of Foods and Nutriments. ("Unsere Nährungs-Chemie: ein Beitrag zur Futter und Nährungs-mittel lehre"). By Emil Pott. Munich: Theodor Ackermann. 1895. 8vo., pp. 104.

The author, whilst duly recognising the value of the initial steps taken by Boussingault and Liebig towards a chemico-physiological development of the principles of animal nutrition, complains, with the fullest right, that we have come to a lamentable stand-still. The attempt to decide summarily on the nutritive value of the different foods according to their percentage of certain constituent groups is, he reminds us, as one-sided as that to determine the fertility of a soil simply by the proportions of nitrogen, potassium, and phosphoric acid. He submits the following propositions:—In order to determine the value of a food, it is necessary to ascertain in what forms it contains those substances which directly or indirectly take part in the nutrition of the animal body. Nor must we forget that we have not yet even an approximate knowledge of the individual constituents of foods.

The nutritive effect of a food varies according as it is to be supplied to ruminants, to horses, or to swine. Nor must the physical structure of a food be neglected.

Different races, and even individuals of one and the same race, have a different power of utilising food.

The value of the constituents of food is very unequal, according as the animals consuming them are destined to yield milk, flesh, fat, to exert mechanical power, or are reserved for propagation.

Finally, before we can decide on the nutrient value of any substance, we must learn in what state or admixture it is supplied for consumption.

The author shows that digestion is a far more complicated process than it is commonly supposed. In addition to that form of digestion effected by the secretions of the animal concerned, there is also a "microbic digestion," effected by the micro-organisms which accompany the food, especially of the herbivora. We have never met with an account of the results of a course of experiments made—or proposed to be made?—by Pasteur to decide on effects of diet completely sterilised.

In connection with these propositions, the author puts forward a number of interesting questions concerning the known action of minimal quantities of certain foods or condiments. Here there is urgent need for careful experimentation. This brings Herr Pott to the question of the flavours and odours of foods, and to the consumption of articles which can scarcely be comprised under the two categories of frame-foods or heat-foods. The recent outcry against so-called excitants or stimulants (coffee, beer, wine, &c., in the case of man) applies also to the lower animals, and with equal injustice. Von Pettenkofer, in reply to the agitators who proscribe all "stimulants," irrespective of proportion, points out that these substances act like lubricants in machinery, which do not enable us, *e.g.*, to dispense with steam-power, but increase its efficiency and save the machinery from needless wear and tear. The common sense of mankind has shown us—as the author quotes from C. von Voit—that what we eat with repugnance, or even with indifference, is of little value to the system.

This little book is so full of passages which suggest, not merely reflection, but experiment, that we must here conclude our scrutiny. We can merely glance at a passage in which it is pointed out that "irrigation hay" is deficient, not merely in odoriferous appetising principles, but also in albumen and phosphoric acid.

CORRESPONDENCE.

ON THE INADEQUACY OF AIDS AND FACILITIES FOR SCIENTIFIC RESEARCH.

To the Editor of the Chemical News.

Sir,—I have just read in the Chemical News (vol. lxxii., p. 224) that, in eulogising very deservedly the work of Professor Runge, it was remarked by Dr. Johnstone Stoney that "it would be very advisable at this juncture to call attention to the unfortunate position in which scientific investigation in the British Islands stood in comparison with that of at least one other country in Europe. There was no scientific man in these islands who possessed a laboratory furnished with the appliances for carrying on such investigations as those which had just been placed before the meeting." "An apparatus which would measure the half or the third of a tenth-metre would really do nothing in an investigation of this kind; they must procure apparatus like the splendid apparatus in Hanover, which would measure to the fiftieth part of a tenth-metre with certainty."

Dr. Armstrong (intervening) said he should like, on behalf of the chemists, who had not said anything up to that time, to express the universal admiration which they must all have of the communications just made to the meeting. He had risen at this juncture not merely with the object of saying this, but also in order to correct the impression which Dr. Johnstone Stoney had just endeavoured to make at the instigation of Professor Lodge, that they were not capable of doing this kind of work in the British Isles." The Doctor went on to say that this work had been done by individual effort after the fashion usual in England. "If the idea of making such investigations as these occurred to men in this country, who had the requisite capacity for undertaking them, he was sure the effort would always be made."

I can quite appreciate the justice of the remarks of Dr. Johnstone Stoney, than whom no one could be better qualified to speak on this subject, of the small encouragement and the inadequacy of the aids given to such scientific investigations in Great Britain and Ireland.

According to my experience Dr. Armstrong was not happy in his remarks.

It must be now some eight or ten years since Dr. Johnstone Stoney and I had a conversation on the desirability of having a 20-foot Rowland concave grating mounted in Dublin, and fitted with all appliances for the investigation of spectra. Such an apparatus being necessary for the determination of certain physical constants, ought certainly to be provided. There were no funds and no building available. This has a bearing on the following circumstances:—In March, 1882, there was published in the *Journal of the Chemical Society* a paper of mine, entitled "Note on Certain Photographs of the Ultra-violet Spectra of Elementary Bodies," in which it was shown that by photographing the spectra of certain well-defined groups of elements in series, the grouping and the characters of the principal lines are referable to the Periodic Law.

This paper was merely the preface to two others; the first, "On Homologous Spectra," published in September, 1883, in the *Journ. Chem. Soc.*; the second, "On the Spectrum of Beryllium, with Observations relative to the Position of that Metal among the Elements," published in June, 1883. Owing to some untoward circumstance the former paper, which was read first, was long delayed in publication, and finally an uncorrected proof was printed. On drawing attention to this, the remark was casually made to me that it did not matter, as no one would ever read the paper.

It is now necessary to mention that this paper contains the following passage with reference to homologous spectra—that is to say, those spectra which are similarly constituted:—

"*The foregoing data present a considerable addition to the body of evidence in support of the view that elements whose atomic weights differ by a constant quantity, and whose chemical character is similar, are truly homologous, or, in other words, are the same kind of matter in different states of condensation. Their particles are vibrating in the same manner, but with different velocities.*" (See "British Association Report, 1883").

J. R. Rydberg, in 1890, contributed to the *Transactions of the Royal Academy of Sweden* a paper entitled "Recherches sur la Constitution des Spectres d'Emission des Eléments Chimiques," in which he states that among the special contributions to the knowledge of the constitution of spectra, "the observation of M. Hartley upon the constant differences of the number of the oscillations of the components of the double rays of an element is of very great importance."

M. Rydberg had remarked upon the double rays of a number of elements in 1885, but recognised the fact that I had already called attention to this subject; and he then enunciates the law as follows:—

"The difference between the oscillation-frequencies (or numbers proportional to them) of the component of a double ray is constant for all the double rays of the same species in the same element." He adds the words, "this relation applies also to the components corresponding to triplets." My paper dealt with triplets and other groups, as well as with double lines; it further treated of rays with certain characters in common; hence it became necessary, in order to include the cases of triplets, to modify the statement of the law.

Mr. J. S. Ames, in the *Phil. Mag.*, vol. xxx., p. 33, 1890, recognised the law of homology in the spectra of the elements as pointed out in my paper, and to him, as well as to M. Rydberg, my thanks are due. M. Rydberg, however, remarks that, as Mr. Hartley has not made further use of the excellent materials which he has obtained by his measurements in the ultra-violet spectra, it may be concluded that he has not attributed much importance to the relations found. The previous quotation, which for the purpose of easy reference is in this letter printed in italics, will, I think, show that I was fully alive to the importance of the facts observed, and, indeed, at a later date it led to the enunciation of the following modification of the Periodic Law:—*The properties of the atoms are a periodic function of their masses;*" and, further, it led to the view which I have taken care to inculcate at various lectures during the past ten years, that, in well-defined groups, the properties of the atoms are absolutely a function of their masses.

In other words, *one element in a group differs in its properties from another, not because it consists of another kind of matter, but because the quantity of matter in an atom of it is different.*

No one can study homologous spectra without being convinced of the enormous importance to the chemist of a thorough investigation into their constitution. To this end it was my particular desire to obtain the use of a large dynamo and gas-engine for producing arc spectra on an adequate scale, and by Rowland's method to photograph them for the purpose of carefully studying the numerical relations between the oscillation-frequencies of similarly constituted groups of lines both in arc and spark spectra. For some time there seemed to be a prospect of the Science and Art Department supplying the electric current suitable for such researches; but it was found that, even had this been done, there was no place within the Royal College of Science where the grating could be mounted and used.

An application was made to the Committee of Section B of the British Association, when it met at Southampton, for a sum of money in aid of the investigation of arc spectra of the elements; but this was not granted. I had already spent a considerable sum in such researches, and had used, for instance, a 6 foot concave grating, but it was found to be of little value.

After fruitless endeavours to obtain the means to carry on the work in a proper manner, the projected investigation went into abeyance. In the meantime Messrs. Kayser and Runge commenced their work "Ueber die Spectren der Elemente." In the *Fierte Abschnitt*, 1891, they refer to my previous investigation, and of course have greatly extended it.

The recital of the foregoing facts will, I think, be found contradictory to the statement of Dr. Armstrong, which, as he admits, was intended to reverse the effect of Dr. Stoney's remarks, and which happened to be singularly inappropriate.

The assistance which I had sought in more than one quarter was not forthcoming, and it certainly appears as if this was due to a want of appreciation among chemists in England of the importance to be attached to an accurate study of spectra.

I may add that it has been a source of the greatest pleasure and satisfaction to me, for the last four years, to observe that the results published by Professors Kayser and Runge have realised what I had been led to expect from observations made years ago with the imperfect means at my command.—I am, &c.,

W. N. Hartley.

Royal College of Science, Dublin.
November 9, 1895.

CANE-SUGAR AND CITRIC ACID.

To the Editor of the Chemical News.

Sir,—If your readers will kindly compare my three notes on this subject with that published by Messrs. Searle and Tankard (Chemical News, vol. lxxii., p. 235), they will see that these gentlemen, who profess to have repeated my experiments, have not done so at all, or at least only partially and unsuccessfully.

I hope to publish later a more complete account, but I have not been able to work for more than six weeks past. I may state, however, that according to the respective quantities of permanganic acid and sugar, according as sulphuric or nitric acid is used, and according to the temperature of the day, the products vary considerably.

In my experiments tartaric acid, citric acid, saccharic acid, and formic acid have been certainly produced, and the two first have been separated and crystallised from alcohol. It is perhaps needless to add that citrate of lime is not precipitated by boiling unless the liquid is of a proper degree of concentration and neutral.

It would be interesting if Messrs. Searle and Tankard would tell us what becomes of the sugar in their experiments. If they do not get the acids I have mentioned, what do they get?—I am, &c.,

T. L. Phipson, Ph.D.

The Casa Mia Laboratory, Putney,
November 16, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Zeitschrift fur Analytische Chemie.
Vol. xxxiv., Part 2, 1895.

Reagent for Monovalent Alcohols.—Bela von Bitto (*Chemiker Zeitung*).—The author mentions that Schönn's reaction takes place only with absolute alcohol, whilst the reactions of Lieben and Landwehr indicate other substances. Hence he proposes a solution of 0·5 methyl violet in 1000 c.c. water. He adds 1 to 2 c.c. of this solution to the liquid in question, adds ½ to 1 c.c. of the solution of an alkaline polysulphide, and shakes up. In presence of monovalent alcohols the liquid turns cherry-red to violet-red, and remains clear. If no monovalent alcohols are present the solution takes a greenish blue colour, and after some time deposits reddish violet flocks, whilst the supernatant liquid becomes yellow. Bi- and polyvalent alcohols, carbohydrates, acids, aromatic compounds, phenols, &c., do not yield this reaction. With methylic and ethylic alcohols, normal and isopropylic alcohol, the colour is a cherry-red; with tertiary butylic alcohol, isobutylic alcohol, isobutylcarbinol, and allylalcohol the colour is a violet-red.

Comparative Studies on the three Isomeric Nitrobenzoïc Acids. — Oechsner de Coninck. — From the *Comptes Rendus.*

Distinction between Aldehyds and Ketones, especially Aldehydic and Ketonic Sugars.—From the *Comptes Rendus.*

Differences in the Behaviour of Tannin Substances with Reagents.—R. Procter (*Der Gerber*).—The author divides the tannins into the following four classes:—Those related to pyrocatechin; those of mixed or unknown origin; those derived from pyrogallol; and those containing ellago-tannic acid. As reagents he uses the following solutions:—(*a*) Iron-alum, a 1 per cent solution, instead of ferric chloride; the colour produced is observed *at once.* (*b*) Bromine water added to the tannin solution until it smells distinctly of bromine, observing whether a precipitate is produced or not. (*c*) Copper sulphate, a 1 per cent solution in slight excess, observing whether the precipitate is soluble in ammonia or not. (*d*) Nitrous acid; to a few c.c. of the dilute tanning solution there are added a few crystals of potassium nitrite and then 3 to 5 drops of decinormal sulphuric or hydrochloric acid. The solution is either at once red, and passes through violet slowly into deep indigo-blue, or there appears only a yellow or brown colouration or a precipitate (see tables). (*e*) Stannous chloride and hydrochloric acid; 10 c.c. of the concentrated solution is added to 1 c.c. of the solution of the tannin; the colour is observed after standing for ten minutes. (*f*) Pine shavings and hydrochloric acid. *Reaction for Phloroglucol.*—A shaving of pine wood is moistened with the tanning solution, and, when dry, is moistened again with concentrated hydrochloric acid; in presence of phloroglucol, there appears at once a light red colour; catechin and gambier give the reaction distinctly. (*g*) Sodium sulphite; to a few drops of the solution of tanning matter there is added a crystal of this salt; with valonia, there appears at once a purple-red colour. (*h*) Concentrated sulphuric acid; a small test-tube is rinsed out with the solution of tannin, which is then poured out so that only a small drop remains, and the sulphuric acid is cautiously substratified. The coloured ring at the plane of contact is observed, the liquids mixed and diluted with water. (*i*) Lime water; the reactions are preferably obtained in a porcelain capsule; an excess of the reagent is not injurious, but it must then be allowed to stand for some time. The strength of the tannin solution must be so adjusted that 0·6 grm. solid residue are contained in 100 c.c. The author's observations are given in detail in the form of tables. Upon them follow, also in tabular form, the earlier observations of Andreasch.

Detection of Hydroxylamine.—A. Angeli (*Gazz. Chimica Italiana*).—The author mixes the neutral solution with sodium nitroprusside and renders it strongly alkaline with soda-lye. On applying heat there appears at once a fine magenta colour. An excess of ammonium salts interferes. Hydrazin and other inorganic reducing agents do not give the above reaction. Phenylhydrazin gives in the cold a red colour, which disappears on heating.

Elementary Analysis of Highly Volatile Organic Substances.—G. Perrin.—The author makes use of a special apparatus resembling that used by Zulkowsky and Lepez for halogens and sulphuretted substances.

Quantitative Determination of Hydrazin in its Salts.—Julius Petersen (*Zeit. Anorg. Chemie*).

Determination of β-Naphthol.—Küster (*Berichte*).—The author appends a table of corrections to his former method.

Volumetric Determination of Naphthalin, Acenaphthen, α- and β-Naphthol, and Analogous Substances.—F. W. Küster (*Berichte*).—The author's method depends on the circumstance that these substances form insoluble compounds with picric acid.

Determination of Antipyrin.—F. Schaak (*American Journal of Pharmacy*).—The author has devised a colorimetric process depending on the formation of nitroso-antipyrin; its bluish green colour can be recognised in dilutions of 1 : 20000.

Gravimetric Determination of Sugar with Fehling's Liquor.—G. Gaud.—From the *Comptes Rendus*.

Determination of the Atomic Weight of Bismuth.—R. Schneider.—From the *Journ. Prakt. Chemie*.

Atomic Weights of Nickel and Cobalt.—R. Schneider.—The mean value obtained for nickel is 58·7433, and that for cobalt 59·3507.

MEETINGS FOR THE WEEK.

Wednesday, 27th.—Society of Arts, 8. "Locomotive Carriages for Common Roads," by H. H. Cunynghame.

THE CHEMICAL NEWS.

Vol. LXXII., No. 1879.

ON THE ATOMIC WEIGHT OF HELIUM.

By N. A. LANGLET.

Although the unitary character of helium may still appear questionable, it will be not uninteresting to obtain an approximate determination of its atomic weight, or at least of the mean atomic weight of its constituents, in order thus to obtain some light on the position of this peculiar substance with relation to known elements. After succeeding in obtaining pure helium, *i.e.*, a gas which displays in Geissler's tube only the spectral lines ascribed to the hypothetical solar element "helium," I have undertaken a determination of its density as accurately as the small quantities of the gas at my disposal permitted.

The helium used in the determinations was prepared and purified as follows:—A tube of a metre in length, of sparingly fusible glass, was charged with a layer of manganese carbonate of 10 c.m. in length, and then filled up almost to one-half with a mixture of (3 parts) pulverised clèveite and (2 parts) potassium pyrosulphate. At about 20 c.m. from the mouth a plug of asbestos was introduced, and the tube was then filled with a stratum of 10 c.m. of coarsely granular copper oxide. After the mixture was spread out in the tube, the copper oxide was heated to redness, and the air, as far as possible, expelled by carbonic acid. The mixture was then heated for a few moments in its entire length, and the gas evolved at first was expelled by carbonic acid to remove any air which might be present. The mixture was then, as in organic analysis, slowly heated to full redness (commencing at the front), and the gas which is briskly evolved was collected in an apparatus resembling Schiff's nitrometer over potassa-lye at 50 per cent. In order to be freed from the last traces of nitrogen, hydrogen, and water, the gas was passed through a long tube of 1 c.m. in thickness (of sparingly fusible glass) which contained, in succession, layers of copper oxide, phosphorus pentoxide, and powdered magnesium. The copper oxide and the magnesium were heated to strong redness. From this tube the gas passed directly into a glass globe holding 100 c.c., and previously carefully exhausted. In this manner the density was found to be 0·139 (air = 1), or 2·00 (H = 1). After weighing, the globe was evacuated, the gas pumped back into the gasometer, and again led through the ignited tube into the globe. The weight of the gas had not varied, and the density was again determined as 0·139. A small quantity of the gas was passed from the globe into a Geissler tube, and its purity was tested spectroscopically. It was found perfectly free from nitrogen, hydrogen, and argon. A determination (made by opportunity of an examination of the specific heat of helium) of a quantity of the gas obtained and purified by the same method gave the value 0·140. Though these determinations cannot claim any great accuracy, on account of the small quantities of the gases employed, we may, without much error, fix the specific gravity at 0·14 (air = 1), or 2·0 (H = 1).

The atomic weight will then be either 2 or 4, according as the mol. contains 2 or 1 atoms. To decide this question, the speed of sound in helium was determined, and from this the proportion was calculated between the specific heat at a constant pressure and at a constant volume. For this purpose the gas was placed in a tube closed at one end by means of a perforated caoutchouc stopper. Over the other end a membrane of caoutchouc was extended air-tight, upon which a plate of glass was cemented with tallow. The tube was then evacuated by means of a narrow tube inserted in the caoutchouc stopper and filled with helium. After the glass plate had been removed, a powerful stream of air was directed rather obliquely through a narrower tube against the membrane, and thus sounds were obtained, the wave-lengths of which could be measured by means of some silicon dioxide introduced into the tube and set in motion by the vibrations. From the speed of the sound found in this manner the relation between the two heat capacities was calculated as 1·67. The low density of helium renders the determinations uncommonly difficult and somewhat uncertain.

The molecule of helium contains, therefore, like that of argon, only 1 atom. The atomic weight must therefore be taken as = 4.

Ramsay, after having in a preliminary communication indicated the specific gravity of helium as 3·88 (H = 1), has lately published an extended examination of the helium obtained from different minerals. The numbers which he obtains do not differ greatly from each other, the mean of all the determinations being 2·18, *i.e.*, 8 or 9 per cent higher than the value which I have found. If helium, as Lockyer and Deslandres have assumed, is not a simple gas, but a mixture of several, the difference would be easily explained. But as Ramsay appears to have made no spectroscopic examination of the purity of the helium which he experimented upon, it is naturally not impossible that, in spite of careful purification, it may have retained slight impurities of nitrogen or argon. If the density which I have obtained can be regarded as correct, Ramsay's helium would contain a mean of 1·5 per cent by volume of nitrogen, or 1 vol. per cent of argon.

When this research was undertaken, Ramsay had obtained from his clèveite merely a mixture of helium with argon, and it seemed not possible to separate both gases from each other. But as I obtained pure helium (as far as it can be ascertained with the spectroscope) from the mineral at my disposal, and it was scarcely possible to assume that the argon studied by Ramsay could be found to be derived from the atmosphere, its absence can be attributed only to an accident which may possibly never recur.

I submit that by these circumstances the apparent intrusion into a region which belongs to the discoverer of helium will be explained and permitted.—*Zeitschrift für Anorganische Chemie*, x., p. 287.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 250).

Chapter II.

On the Nature and Amount of Soluble and Insoluble Mineral Matters, in the Air at the Higher District of Brussels, and in Rain Water, at given times and under given conditions.

One knows, from researches made in different places at given times, that air may contain soluble and insoluble compounds of sodium, calcium, and potassium, together with many insoluble silicates. The late Robert Angus Smith reviewed our knowledge of this subject in his standard work "Air and Rain." *

Judging by the very great trouble experienced during spectroscopic observations of flames burning in the air of Brussels and the neighbourhood, one is tempted to believe in the existence of large quantities of sodium compounds, such as sulphates and chlorides, in the air of this town. Researches that I have undertaken at very different periods have convinced me that this opinion is erroneous,

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* "Air and Rain," by Robert Angus Smith. London: Longmans and Co. 1872.

at least as regards the higher part of the town, where my experiments were made. As a matter of fact, when taking from *ten to fifteen cubic metres* of air as a unit of volume, one cannot measure the amount of soluble sodium compounds present. It is not so with insoluble compounds of sodium and calcium.

In order to ascertain the quantity of solids suspended in free air, when it was *as still as possible*, I condensed the water vapour which exists in such variable quantities. It seemed to me, in fact, that, *during the process of condensation, the water ought to entrap all particles, of whatever material, suspended* IN THE LAYER OF AIR IN CONTACT *with a surface chilled below dew-point.* I effected this condensation on the outer surface of a polished platinum apparatus which had been recently washed and then heated to redness. The apparatus I used consisted of a cylindrical platinum refrigerator with a domed top, 20 c.m. diameter by 30 c.m. height.

The domed top, fitting loosely on the vessel, reached 2 c.m. down it, and was provided with a long collar and a large tube in the centre. The vessel was two-thirds filled with disulphide of carbon; in the opening in the lid was fitted a cork, pierced by a glass tube for bringing a current of dry air to the disulphide of carbon, and by a thermometer registering $\frac{1}{50}$th of a degree C.. The air current was made by bellows or a water-pump, and was dried before reaching the disulphide of carbon. When the water-pressure was constant, the bellows were able to regulate the current so as to obtain and keep a sufficiently low temperature to bring the walls of the vessel below dew-point, and as near as possible to 0° C., without freezing the condensation water.*

To the collar of the domed top was fitted a cork pierced by a glass tube, meant to conduct away the air saturated with disulphide of carbon vapour.

During use the apparatus was freely suspended in a slightly inclined position, in order to assist the fall of the water. A platinum sheet served to lead the water, as it was condensed, into a platinum funnel containing a double filter-paper washed in succession with dilute nitric acid, with pure water, with dilute hydrofluoric acid, and again with pure water, touched at one point the lower part of the bottom of the vessel.

The spout of the platinum funnel passed through a hole in a glass plate which supported the funnel, and was itself supported by a small platinum dish recently washed and ignited to redness, meant to receive the filtered water of condensation.

I then ascertained the amount of water collected, by weighing it in a covered platinum crucible.

To determine the nature and weight of the bodies left in the filter, I made the following arrangements:—

Into a platinum dish, of 110 cubic c.m. capacity, previously washed and ignited to redness and furnished with *a spout*, was measured *one hundred grms.* of filtered water, which was then evaporated on a bath. When the water was evaporated down to about 1 c.c., the liquid was transferred into a very small well-polished platinum dish, weighing about *one grm.*, and the weight of which I had determined to within *two or three thousandths of a m.grm.* After evaporating the liquid from the very small platinum dish on the bath, I put into it the washings from the larger dish, and evaporated the whole to a constant weight. I then weighed and determined the nature of the residue. I tested for chlorides with nitrate of silver, and for sulphates with chloride of barium.

The filters, through which the condensation water had been passed, were then dried. The inner filter was compared with the outer, and both were examined under a microscope. After this examination the inner filter was folded and re-folded and tied in a fine platinum wire, and carbonised at a low temperature *in a closed platinum vessel.*

The carbon was carefully put into the outer envelope of a gas jet, to burn it. During combustion one could ascertain, by spectrum analysis, the nature of the spectrum produced.

After combustion I weighed the ash, and determined its constituents by using successively *chloride* of ammonium, *fluoride* of ammonium, and sulphuric acid, all pure.

The results arrived at were as follows:—

A. *Outer Air.*—The condensing apparatus was freely suspended outside a window with a south-west exposure, looking on to a garden, 9 metres above the ground, which is 49 metres above the lower part of the tower and 77 metres above sea-level, at about 45 c.m. from the wall,—and a board was used to support articles to be placed outside the window. The apparatus was sheltered from wind from the front and sides, from sun, and rain, by movable screens, also 45 c.m. away from it. Nevertheless the surrounding air could freely penetrate from above and below, as well as circulate in and escape from this enclosed space.

A Bunsen lamp, which could be lighted from inside by opening one of the movable window-panes, was put on the board. This lamp was surmounted by a very large sheet-iron funnel, communicating with a sheet-iron pipe fixed to the wall, to carry off the products of combustion of the coal-gas feeding the lamp. By opening the movable pane in front of the lamp, and bringing forward the spectroscope, one could at any time make a spectrum analysis of the flame, which assisted, as I satisfied myself, to a great extent in the supply of air to the enclosed space.

A thermometer *in the shade*, and identical with that in the top of the apparatus and reaching into the disulphide of carbon, showed the outside temperature.

Having made all arrangements for my experiment, I started the pump *slowly*, so as to bring dry air through the disulphide of carbon and lower the temperature to dew-point. Owing to the considerable size of the apparatus and the care I took, I was able, at every attempt, to fix this point to within about 0·2°.

1st. With a light west wind:—

Temperature of the air	18·5°
Dew point	12·6°
Weight of water condensed ..	125 grms.

Whilst the pump was working, the temperature of the disulphide of carbon was between 0° and 3°, and an analysis of the flame of the Bunsen lamp showed a decided sodium spectrum.

Five drops ($\frac{1}{5}$ c.c.) of a 10 per cent solution of nitrate of silver had a perceptible effect on 10 c.c. of the filtered water contained in a stoppered glass tube, with its bottom flattened and polished, 15 m.m. diameter, and surrounded for its whole length by paper blackened with lamp-black,—a condition in which the least opalescence is easily noticed.

One drop of a saturated solution of chloride of barium had no effect on *ten c.c.* of the filtered water. After evaporating the mixture down to about half a c.c., the liquid was perceptibly clouded.

The evaporation of 100 c.c. of the filtered water, on a bath *in the outer air*, left a small yellowish transparent stain, perceptibly hygroscopic, the weight of which was less than the limit of error of weight,—that is, two or three thousandths of a m.grm.; when heated, this residue perceptibly blackened; when dissolved in a few drops of pure water, it made a solution of which a part, when put on to a fine platinum wire loop recently ignited to redness was entirely volatilised, colouring a Bunsen jet yellow, and showing on analysis a *brilliant*, though temporary, sodium spectrum without a trace of a calcium spectrum,

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* During these experiments, when the pressure of the water working the bellows was increased, the water of condensation, instead of being deposited in a liquid state, was frozen. The ice produced was either quite *transparent* or *opaque*, but tinted either with *black*, like smoky quartz, or with *yellowish gray*. An examination under the microscope of this ice, or of the water got by melting it, plainly showed the shape of the foreign bodies mixed with it. I call the attention of any one engaged in researches on the nature of the particles floating in the air to this point.

even after having moistened the loop with a solution of chloride of ammonium.

The inner filter, through which the condensation water had passed, showed, after desiccation, a greyish tint. With a microscope one could see numerous black specks and bright grey specks, as well as a great number of filaments.

The introduction of the carbon, made by carbonising the inner filter in a closed vessel, into the envelope of a Bunsen jet, coloured a great part of it yellow.

During the combustion of the carbon, spectrum analysis showed a sodium spectrum, and a faint and incomplete calcium spectrum, but no trace of the potassium line. The weight of the deep brown siliceous ash was about 0·000085 grm.

The ash, when dissolved in a saturated solution of chloride of ammonium adhering to a fine platinum wire loop, and introduced, after slow desiccation, into a Bunsen jet, showed a strong sodium spectrum and a faint calcium spectrum. but no trace of the potassium line.

The loop, coated with the ash, was moistened thrice with a saturated solution of volatile *fluoride of ammonium*, heated each time to a dull red heat, to volatilise the siliceous sand and the silica from the silicates, and then put into the envelope of a Bunsen flame; it immediately coloured it yellow. Spectrum analysis of this envelope showed the sodium line, but no trace of a calcium or potassium spectrum.

The platinum wire loop, when moistened with sulphuric acid and put into the flame, coloured it yellow, but spectrum analysis of the flame did not show the potassium line.

Thus the water of condensation contained a trace of sodium in the form of chloride and sulphate, and sodium and calcium in the form of various silicates, whilst silicate of potassium was not present.

2nd. With a total absence of wind :—

Temperature of the air .. .. 8·20°
Dew-point .. .. 7·95°
Condensed water .. .. .. 125 grms.

At the time of commencing to condense the vapour, fine rain had alternated for three days with damp fog, and the sheltering screens were quite damp. During the time occupied in condensing, which was considerable, the temperature of the disulphide of carbon varied from 0° to 2·5°, and spectrum analysis of the flame burning in air failed to show the sodium line.

Five drops of the 10 per cent solution of nitrate of silver, after waiting for thirty minutes, produced no cloudiness in 10 c.c. of filtered water. When the volume of the mixture was reduced by evaporation to about half a c.c., a cloudiness appeared on cooling it. This was re-dissolved by ammonia.

The liquid formed by the evaporation of 10 c.c. of filtered water down to about half a c.c., was slightly clouded by one drop of a saturated solution of chloride of barium.

One hundred c.c. of filtered water left, on evaporation, a small brown stain, quite distinct under a microscope, and perceptibly hygroscopic. The weight of it was within the limit of error in the weight of the dish (0·003 m.grm.). The stain perceptibly blackened when heated; the residue was dissolved by two drops of water, and the solution, when put into a Bunsen flame, showed the sodium line *only*.

When the inner filter through which the water passed was dried, it was decidedly grey; when examined under a microscope, it showed numerous small black specks, and also filaments of various lengths. Combustion of the carbon, made by carbonising the filter in a closed vessel, left a trace of decidedly brown ash. During the whole period of combustion I saw the sodium spectrum to the exclusion of any other.

Thus, although I was not able by spectrum analysis to detect the presence of the sodium line in the Bunsen flame burning in the air which furnished the water of condensation, I nevertheless ascertained that it contained sodium in the form of chloride and sulphate, since the water of condensation contained a trace of these bodies.

3rd. Favourable atmospheric conditions occurring, I checked these latter observations. After *five* days' drizzle, *without sensible wind*, and whilst it continued raining,—

The air temperature being.. .. .. 9·45°
And the dew-point .. .. 9·15°
I collected by condensation 135 grms. of water.

The screens sheltering the apparatus were thoroughly soaked by the rain. Throughout the time the apparatus was working, the temperature of the disulphide of carbon was between 0° and 2·8°. Spectrum analysis of the Bunsen flame burning in the outer air did not show a glimpse of the sodium line.

Five drops of a 10 per cent solution of nitrate of silver in 10 c.c. of filtered water showed no appreciable precipitate after waiting twenty minutes. When the mixture was evaporated down to about half a c.c. it perceptibly clouded on cooling; this was re-dissolved by ammonia.

Ten c.c. of filtered water were evaporated down to about half a c.c. The liquid was *slightly* clouded by one drop of a saturated solution of chloride of barium.

One hundred c.c. of filtered water left, on evaporation, a small sparkling brown stain, absolutely unweighable. When heated, the stain turned black; the residue, when dissolved by two drops of water, and put, in the form of a solution, into a Bunsen flame, coloured it yellow. Spectrum analysis of the flame showed a brightly-coloured, but temporary, sodium line.

The inner filter through which the water passed, when dried and compared with the second filter, also dried, had a distinct grey tint on the side which received the water, and showed under the microscope a number of black specks, and also filaments, some long, others short. After burning the carbon made by carbonising the inner filter, there remained a minute trace of brown ash. During the combustion I saw a very faint and transient sodium spectrum.

Thus, although I was not able at any time to detect the sodium line in a Bunsen flame burning in the air, nevertheless the air contained sodium in the form of chloride and sulphate, but in an absolutely unweighable quantity in 15 cubic metres of air.

(To be continued).

THE QUANTITATIVE DETERMINATION OF PERCHLORATES.*

By D. ALBERT KREIDER.

(Concluded from p. 252).

It is necessary of course to prevent the access of air into the bulb until the acid has been neutralised, to accomplish which, without loss of iodine, potassium carbonate must be used, at least for the end reaction. To remove the contents of the bulb for titration the two delivery-tubes were filled with water, after removing all sodium hydrate from the one through which the oxygen was entered; the shorter end connected to a supported funnel containing a saturated solution of bicarbonate, and the longer one inserted into an Erlenmeyer beaker containing a saturated solution of bicarbonate in amount sufficient—as previously determined—to neutralise all the acid taken. By opening that stopcock the delivery-tube of which reaches below the liquid in the beaker, the bicarbonate is drawn in by the partial vacuum, with liberation of sufficient carbon dioxide to force all the

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* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. l., October, 1895.

liquid out. Owing to the consequent effervescence as the liquid gains its exit, the flow must be regulated by the stopcock so as to avoid loss of iodine, which is prevented by inclining the beaker so that the bubbles strike against its side instead of being allowed to splatter out of the opening. To wash out the bulb it is raised almost horizontally, so as to prevent the liquid from running through, and the upper stopcock opened to admit the bicarbonate from the funnel. Both stopcocks are then closed, the bulb disconnected and agitated, after which it may be washed with water and admission of air without any fear of liberating more iodine. An excess of decinormal arsenic is then run into the beaker and titrated back with iodine.

The many little precautions essential to note for the manipulation are in practice accomplished in a few moments. Seven determinations (not counting one which was all but completed, when an accident terminated it), from the weighing of the perchlorate to the titration, were completed in one day: and the results recorded in Table VII. show with what reliability. In making the series of experiments recorded in Table VII. it was found expeditious to have a partial vacuum always accessible instead of waiting each time for the exhaustion. This was obtained by connecting a vacuum flask with a two-holed stopper to an ordinary water-pump, and having the other perforation fitted with a glass stopcock. The bulb was merely attached to the vacuum by a piece of rubber tubing; the stopcock opened and closed immediately, by which means a sufficient exhaustion was secured. To have the vacuum always in readiness, a valve, described in a former article of mine (*Amer. Journ. of Science*, l., p. 132), was placed in the rubber leading to the pump, and when lubricated with glycerin would hold the vacuum perfectly. The nitric oxide employed was supplied by a Kipp generator, in which globules of copper were acted upon by nitric acid mixed with an equal volume of water. To purify the gas evolved from any possible trace of the higher oxides, it was first passed through an acidified solution of potassium iodide in Geissler absorption bulbs, the latter one of the three being alkaline. This method of generating nitric oxide in a Kipp generator (preferably charged with dilute acid and kept warm by immersion in hot water when large amounts of the gas are to be drawn at frequent intervals) was devised by Professor Gooch, by whom it has been employed for some time. It is automatic and eminently satisfactory. The hydriodic acid was obtained from a solution of potassium iodide containing 1 grm. in 10 c.c.; 30 c.c. being taken for each experiment, and acidified with the required amount of hydrochloric acid immediately before using, so as to prevent any liberation of iodine by the oxygen of the air. In those experiments in which more than this amount of potassium iodide was employed a correspondingly stronger solution of the latter was used, so that the volume of water was in all cases 30 c.c.

Table VII.

	$KClO_4$ taken. Grm.	KI taken. Grms.	HCl taken. C.m.^{3}	$KClO_4$ found. Grm.	Error. Grm.
(32)	0·1000	3·0	3·0	0·1003	0·0003+
(33)	0·1000	3·0	3·0	0·1006	0·0006+
(34)	0·1000	3·0	3·0	0·0998	0·0002−
(35)	0·1000	4·0	4·0	0·1003	0·0003+
(36)	0·1000	3·0	3·0	0·1003	0·0003+
(37)	0·1000	3·0	4·0	0·0999	0·0001−
(38)	0·1000	3·0	3·0	0·1003	0·0003+
(39)	0·1000	3·0	4·0	0·1001	0·0001+
(40)	0·1500	3·0	4·0	0·1493	0·0007−
(41)	0·2000	6·0	6·0	0·1999	0·0001−
(42)	0·2000	6·0	6·0	0·2009	0·0009+
(43)	0·0100	3·0	3·0	0·0099	0·0001−
(44)	0·0100	3·0	3·0	0·0100	0·0000
(45)	0·0000	3·0	3·0	0·0003	0·0003+

In experiments (40) and (43), during a momentary pause in the shaking of the bulb during the absorption, a black deposit of iodine began to form on the glass, and the result proves the importance of the precaution previously given, that the hydriodic acid should be kept hurling about the bulb until the action is completed. The blank determination (45) shows a constant error of the process, which is about 0·0003+, and will be seen to correspond very closely to the average error of the determination. The cause is doubtless to be attributed to the trace of air which may remain in the bulb or be dissolved in the water. Since it can easily be determined and the correction made, it does not detract in any degree from the reliability of the determination.

To determine perchloric acid associated with other oxidising agents, it is only necessary to treat the mixture with the reagents which this investigation and the one referred to has shown to accomplish the reduction without affecting the perchlorate; subsequently evaporating to dryness and treating the residue according to the above process, viz., by heating in a current of carbon dioxide until decomposition is complete; collecting the oxygen over caustic potash; allowing it to enter a partial vacuum bulb containing a solution of potassium iodide, hydrochloric acid, and nitric oxide under constant agitation; and determining by means of a standard solution of arsenic the amount of iodine set free. The method is proving applicable also to the determination of oxygen in air, or wherever it may be obtained in the free state, unless diluted to such an extent with other gases that the vacuum would be filled by the diluent; even this contingency could be met by enlargement of the absorption-bulb.

Many helpful suggestions are to be credited to Prof. Gooch.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending October 31st, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, November 11th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 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 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 Oct. 1st to Oct. 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 189 samples examined all were found to be clear, bright, and well filtered.

We have this month to record an excess of rainfall, the quantity measured at Oxford being 2·85 inches, compared with 2·56 inches (the average for 25 years), showing an excess of 0·29 inches. The rain was fairly well distributed throughout the month, though more fell in the first ten days than later on. There were fifteen days on which no rain fell.

Compared with the corresponding month of last year, the quality of the Thames derived waters shows a marked improvement in every respect; and, in spite of a much heavier rainfall than in September last, the results are almost identical.

Our bacteriological examinations give the following results:—

	Colonies per c.c.
Thames water, unfiltered	2603
Thames water, from the clear water wells of the five Thames-derived supplies .. highest	108
Ditto ditto .. .. lowest	30
Ditto ditto .. .. mean	68
New River water, unfiltered	1577
New River water, from the Company's clear water well	41
River Lea water, unfiltered	3018
River Lea water, from the East London Company's clear water well	48

These results show that the Water Companies are able to successfully cope with the extra strain put upon them, their filtering appliances being in excellent condition.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Concluded from p. 251).

The Molecular Mass of Liquid Acetic Acid and a General Method of Determining Molecular Masses of Liquids.

The data given in the preceding section on the vapour-tensions of mixtures of acetic acid and benzene, taken in connection with the fact that the partial tension of benzene in its solutions is directly proportional to its concentration, permit of determining the molecular mass of the acid when diluted to any degree whatsoever with the hydrocarbon; and this special case may be generalised so as to permit of universal application. Furthermore, if the molecular mass of a substance be known in solutions of every degree of concentration, it is possible by a little extrapolation to pass over to the molecular mass of the pure liquid. It is, of course, assumed in making such an extrapolation that no break occurs in the continuity of the phenomenon, that is, the addition of very small quantities of a normal liquid to an associated one occasions correspondingly small changes in the degree of complexity of the molecules of the latter.

The way in which I have gone about to get at the molecular mass of acetic acid in benzene and toluene solution is as follows:—

In a system of co-ordinates, molecular masses of acetic acid from 0 to 100 were laid off on the axis of abscissæ (20 inches long), and on the axis of ordinates, the vapour-tensions were taken from 0 to 150 m.m. of mercury (15 inches long). A straight line was drawn from the point 100 on the axis of abscissæ and 0 on the right-hand axis of ordinates to the point 0 on the axis of abscissæ and 146 (benzene at 35°, 75·6 (benzene at 20°), and 47·2 (toluene at 35°). Upon this straight line must lie all the points corresponding to the partial tensions of benzene or toluene dissolved in acetic acid. So points were marked along it giving the value of the partial tensions of benzene and toluene in solutions containing 10, 20, 30, &c., per cent of acetic acid, the data being taken from Table XIII.

The value of the abscissæ which these points determine give the number of molecules of acetic acid contained in 100 molecules of the mixture. All that has to be done now is to solve for every case this problem: Given a mixture containing m parts of a liquid A, having a molecular mass x, and n parts of a liquid B, having a molecular mass y; the mixture is made up of r molecules of A and s molecules of B. What is the value of x in the terms of y, m, n, r, and s?

In the case before us we will take acetic acid for the liquid A, and benzene, or toluene as the case may be, for B; then n is equal to $(100-m)$ and s to $(100-r)$.

It is easily found that the solution of our problem is—

$$x = \frac{m\,s\,y}{r\,n} \text{ or } x = \frac{m(100-r)y}{(100-m)r}.$$

In the accompanying Tables, XIV., XV., and XVI., the values of m, r, and x are given.

Table XIV.

Molecular Mass of Acetic Acid dissolved in Benzene at 35°.

Per cent of $C_2H_4O_2$ in liquid mixture.	Mols. $C_2H_4O_2$ in 100 mols. of liquid mixture.	Molecular mass of acetic acid.
10	5·2	158
20	10·6	164
30	16·6	167
40	23·1	173
50	30·0	182
60	37·7	193
70	47·2	203
80	59·3	213
90	75·6	227
100	100·0	240

Table XV.

Molecular Mass of Acetic Acid dissolved in Benzene at 20°.

Per cent of $C_2H_4O_2$ in liquid mixture.	Mols. $C_2H_4O_2$ in 100 mols. of liquid mixture.	Molecular mass of acetic acid.
10	5·1	161
20	10·5	166
30	16·2	172
40	22·6	177
50	29·6	186
60	37·2	198
70	46·7	208
80	58·7	218
90	75·2	231
100	100·0	244

Table XVI.

Molecular Mass of Acetic Acid dissolved in Toluene at 35°.

Per cent of $C_2H_4O_2$ in liquid mixture.	Mols. $C_2H_4O_2$ in 100 mols. of liquid mixture.	Molecular mass of acetic acid.
10	6·1	159
20	12·4	163
30	19·0	168
40	26 5	170
50	32·8	188
60	41·3	196
70	51·2	204
80	61·1	213
90	78·4	228
100	100·0	240

Considering Tables XIV. and XVI. first, we see that the values of x are approximately the same, the molecular mass of the acid becoming less and less as it is more and more diluted with benzene or toluene. It is remarkable that these two series of values for x fall out so nearly the same, for in the mixture of toluene and acetic acid the differences of their vapour-tensions is so slight that the line of partial pressures of toluene is nearly horizontal, and an error of one millimetre in the determination of the partial pressure may occasion an error of four units in the molecular concentration; in the mixture of benzene and

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* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

acid, however, the error arising from this source is not more than three-tenths of a unit, the angle made by the line of partial pressures being considerably greater than in the case of the other mixture.

For the determination carried out at 20° on the mixture of benzene and acetic acid, it is seen that the number of molecules of acid is less, and hence their molecular mass is greater than when the determinations were carried out at 35°. This is just what is to be expected, for the lowering of temperature has been found to be invariably accompanied by an increase in the condensation of the molecule.

I have sketched the curves corresponding to the values of m and x given in the foregoing tables in a system of co-ordinates with percentage composition as axis of abscissæ and molecular masses as axis of ordinates.

The curves for the mixture of acetic acid and benzene at 35° practically coincides with that of the mixture of acetic acid and toluene at 35°, while the curve for the mixture of benzene and acetic acid at 20° is parallel and slightly above the other two. The curves are perfectly regular in form, and if prolonged to cut the right-hand axis of ordinates cannot give values varying by more than one unit; accordingly it may be claimed that the point where the axis of ordinates is cut by the extrapolated curve gives to about one unit the molecular mass of acetic acid in the liquid state at the temperature taken for the determinations. The results of my extrapolations gives as the molecular mass of liquid acetic acid at 35°, 240, and at 20° 244.

It is interesting to compare these results with those obtained by Ramsay and Shields ("Ueber die Molekulargewichte der Flüssigkeiten," *Zeit. phys. Chem.*, xii., 470, 1893). These investigators found by the determination of the superficial tension of acetic acid that its molecular mass between the temperature limits, 16° and 46°, was equal to 217·2 (60 × 3·62); although this result leaves room for considerable uncertainty as to what the molecular mass of the acid is at any given temperature between these limits, it is in corroboration of my results; for, as has been well established, the degree of association in the molecules of a complex liquid is greater the lower the temperature, and my results pertain to temperatures which are lower or about the same as the mean of the two extreme temperatures given by the two English chemists.

The method of determining the molecular masses of liquids described in this section is the only one as yet devised which permits of the determination at any given temperature of the mass of the molecule.

It is founded on empirical results and depends upon no hypothesis other than the universally recognised one of Avogadro. It is applicable to all cases where the substances under examination can be accurately analysed. It calls for no special apparatus, even a modest laboratory being provided with the necessary pieces. It requires no great amount of manipulative skill, and the results are obtained in relatively short time. I hope that it will be rigidly tested by chemists, and any omissions of this mere sketch be supplied.

Resumé.

The main results of this article may be summed up as follows:—

1. A method of determining the partial pressures of mixtures of liquids has been elaborated, and its sources of error discussed.
2. Although the method can be said to give the vapour-tensions of pure liquids with an accuracy equal to that obtainable by the best of other methods only when the liquids are not very volatile, the results obtained by it for mixtures of liquids of not too different volatilities are accurate enough to serve as the experimental basis for theoretical deductions and generalisations.
3. A number of mixtures of representative liquids have been investigated as regards their vapour-tensions.
4. In some cases extremely simple relations were found; in others, certain complexities presented themselves.
5. A re-calculation of Regnault's determinations of the vapour-tensions of some mixtures of normal liquids, as well as a consideration of Raoult's conclusions and Brown's work on the boiling-points of solutions, showed that it was permissible to apply what was found true for any one temperature to any other.
6. The relations between the concentrations in the gaseous and liquid phases were found to be quite simple and entirely in accordance with the provisions of the relations established by Planck and Nernst.
7. The changes of temperature occurring when certain liquids were mixed were found to be very small, and the resulting mixtures were those which exhibited the simplest relations in their vapour-tensions.
8. The vapour-tensions of mixtures of acetic acid with benzene and with toluene were determined, and the results were such as to permit of the determination of the molecular mass of the dissolved and liquid acid.
9. A general method for the determination of the molecular masses of associated liquids at any given temperature was developed and illustrated with acetic acid.

The experimental part of this investigation was done in a laboratory in the School of Mines at Paris, placed at my disposition by the authorities of that noble institution; and I here take the pleasant privilege of thanking them for the courtesy thus extended to me. My cordial thanks are also due to M. Emilio Damour, Ingénieur Civil des Mines, for his foreseeing kindness in furnishing me with apparatus and material; especially are my thanks due, however, to M. H. Le Chatelier, Ingénieur en Chef des Mines, whose wise direction and good counsel have been of great value to me throughout the work.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1895.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Messrs. A. F. Fuerst, T. F. H. Gilbard, E. T. Read, and A. Stansfield were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of the Earl of Berkeley, Boars Hill, Abingdon; Messrs. Arthur Jenner Chapman, Burleigh House, Yerbury Road, Upper Holloway; George Bertram Cockburn, B.A., St. George's Hospital, S.W.; Charles Croeker, St. Peter's Road, Cockett, Swansea; Gurney Cuthbertson, 69, Shoreham Street, Sheffield; William Dixon, 102, Spring Street, Bury, Lancs.; Patrick Joseph D. Fielding, 8, St. Joseph's Place, Cork; James Gardner, 80, Heaton Terrace, Middleton, near Manchester; Edward Graham, B.Sc., Dalton Hall, Manchester; Edgar Septimus Hanes, 108, Alexandra Road, St. John's Wood, N.W.; Thomas Hawkins Percy Heriot, 23, Wolseley Road, Crouch End, N.; Frederick Arthur Hillard, B.A., 1, Upper Tichborne Street, Leicester; Arthur Edward Holme, M.A., 3, Ash Terrace, Savile Town, Dewsbury; Alfred James, 18, St. Andrew's Drive, Pollokshields, N.B.; Frederick Edward Johnson, 16, Stanley Terrace, West Park, Hull; Leonard P. Kinnicutt, Ph.D., &c., Worcester, Mass., U.S.A.; Walter Mansfield, Trafalgar House, Broughton, Lancs.; Cecil Massey, Lyndon House, Lenton Boulevard, Nottingham; James McCreath, 4, Lombard Court, E.C.; David James Morgan, 10, Northampton Place, Swansea; Herbert Peck, Wigan Road, Ormskirk; William Round, 45, St. Peter's Road, Handsworth, Birmingham; Clarence Arthur Seyler, B.Sc., 31, Windsor Terrace, Swansea; Matthew Smith, B.A., Aston Hall, Preston Brook, Cheshire; Frank Robert Stephens, Idris and Co., Camden Town, N.W.; George Stone, Sydney, N.S.W.; Albert

Thorpe, Charnwood House, Sleaford Road, Preston; John Williams, B.A., Wesley College, Sheffield; Thomas Rowland Wingfield, 43, Dorset Street, Bolton; William Chattaway, Apothecaries Hall, Blackfriars, E.C.; Martin Priest, Apothecaries Hall, Blackfriars, E.C.; William Oakes Kibble, Norton Villa, Buckhurst Hill, Essex.

The President announced that the following telegram had been sent to Madame Pasteur on the death of her husband, M. Louis Pasteur, in October last:—

"Madame Pasteur, Institut Pasteur, Rue Dutot, Paris.

"The Chemical Society of London, in common with the entire scientific world, mourns the loss of its illustrious Foreign Member, and begs to express to you its deepest sympathy.

"Vernon Harcourt, *President*,
"T. E. Thorpe, *Treasurer*.
"John M. Thomson,
"Wyndham R. Dunstan, } *Secretaries*,"
"R. Meldola,

and that the following Address had been presented on behalf of the Society by Dr. Frankland to the Institute of France on the occasion of its Hundredth Anniversary:—

"The leading men of the French nation in Literature, Science, and Art celebrate to-day the hundredth anniversary of a great event. There had perished in the throes of the revolution a group of Academies which for more than a hundred years had shed lustre upon France, and had contributed among the foremost to the general advance of mankind. It was an eclipse of which the darkness could not last long. Two years later, on the 25th of October, 1795, the law was passed which revived the Academies and combined them in the Institute.

"The Chemical Society of London, born half a century later, and representing one of the sciences which are united under the Académie des Sciences Mathématiques et Physiques, desire on this occasion to record their sense of the splendid additions to chemical knowledge and thought which have been made by members of the French Academy. They respectfully offer to the Institute their congratulations on what has been achieved, to which they must now add their sympathy and regret for those who have passed away, thinking especially of the recent loss which science and humanity have sustained by the death of the illustrious Pasteur.

"*President*, A. Vernon Harcourt.
"*Treasurer*, T. E. Thorpe.
"*Honorary Secretaries*, { John M. Thomson. Wyndham R. Dunstan.
"*Foreign Secretary*, Raphael Meldola."

October 25th, 1895.

Of the following papers those marked * were read:—

*120. "*On Flame Temperatures and the Acetylene Theory of Luminosity*. By Arthur Smithells, B.Sc.

The author has submitted to experimental and critical examination the acetylene theory of luminous hydrocarbon flames advocated by Lewes (*Trans. Chem. Soc.*, 1895, lxi., 322; *Proc. Roy. Soc.*, 1895, lvii., 450), and concludes that it is untenable.

Details of the measurement of the temperatures of different parts of hydrocarbon flames by means of the Le Chatelier thermo-couple are given. It is shown that, to obtain readings of any value, the wires constituting the couple must be bent so as to fit the particular region of the flame in which the meaaurement is desired, and that if the sheet of flame be thin even this precaution is insufficient. The exploration of an ordinary flat coal-gas flame gives evidence of no sudden change of temperature in a vertical plane. Sudden changes are found, however, when the couple is moved from the middle of the flame outwards in a horizontal plane, and the mantle has a temperature higher than the melting-point of platinum.

The author considers Lewes's description of the distribution of zones in flames to be based on erroneous temperature measurements, and finds no evidence of such a local condition of temperature as would point to the decomposition of acetylene. The conclusion in favour of the acetylene theory, based on the comparative luminosity of the ethylene and acetylene flames, is attributed to neglect of the consideration that in the latter there is a higher temperature and a greater relative amount of carbon. The indirect evidence derived from the behaviour of cyanogen is stated to arise from the yellow ammonia flame having been mistaken for one containing solid carbon. The theoretical arguments based on thermochemical considerations are adversely criticised.

The author maintains that the luminosity of hydrocarbon flames, including the flame of acetylene, can be adequately explained on the older theory of their structure confirmed and extended by his earlier experiments (*Trans. Chem. Soc.*, 1892, lxi., 217). According to this view, a luminous flame is invested by a sheath of gas in non-luminous combustion. This sheath, which is double at the lower part, corresponds to the two cones of a Bunsen flame, and produces an exceedingly high temperature. The gas within this sheath is intensely heated as it ascends, and is gradually decomposed so as to furnish a sheet of carbon particles, becoming more and more numerous. These glow partly by heat and partly by combustion; the higher the temperature of the non-luminous sheath, and the greater the relative number of particles, the brighter will be the flame. This is well seen in the case of acetylene. The author believes that the precise steps in the decomposition of a hydrocarbon by which carbon is deposited are at present unascertainable by any direct means, but, as the glow of the carbon particles in a hydrocarbon flame is in no case greater than that acquired by a platinum wire immersed in the same region, he considers that there is no ground for supposing that the endothermic decomposition of acetylene (of which substance only a very small quantity has been found in the flame gases) plays any appreciable part in the phenomenon.

*121. "*A New Series of Hydrazines.*" By Frederick D. Chattaway and Harry Ingle, B.Sc.

Primary and secondary hydrazines have proved such important substances that other substituted derivatives of hydrazine have scarcely been studied.

Theoretically, hydrazine should yield five series of substituted derivatives, of which only three are known, the primary, the secondary symmetrical, and the secondary unsymmetrical. No simple method of obtaining members of the other series has hitherto been described, and the authors have undertaken their investigation.

The quaternary hydrazines, which are dealt with in the paper, can be obtained by a simple general reaction from the secondary amines.

The secondary amine is treated with sodium or sodium ethylate, whereby the hydrogen atom is replaced by sodium, $R_2NH + Na = R_2NNa + H$. The equivalent quantity of iodine is then allowed to act upon the sodium compound, when the sodium atoms are withdrawn, and the two substituted amido-groups unite to form the quaternary hydrazine,—

$$R_2N{\cdot}Na + I_2 + Na{\cdot}NR_2 = R_2N{\cdot}NR_2 + 2NaI.$$

The aromatic quaternary hydrazines which have been so far more especially studied are stable well-crystallised compounds, which are not easily oxidised, and are scarcely, if at all, basic. Their percentage composition, and the molecular weights obtained by Raoult's method, using benzene as a solvent, agree well with the theoretical.

Tetraphenyl hydrazine, $(C_6H_5)_2N{\cdot}N(C_6H_5)_2$, obtained by the above reaction from diphenylamine, crystallises in long orthorhombic prisms, m. p. 147°. It is easily soluble in benzene, chloroform, and acetone, and dissolves in cold concentrated sulphuric acid, giving a deep purple solution.

Tetra-p-*tolyl hydrazine*, $(C_6H_4CH_3)_2N{\cdot}N(C_6H_4CH_3)_2$, prepared from di-*p*-tolylamine, crystallises in large pale yellow monoclinic prisms or tables, m.p. 138°. It is easily soluble in benzene, acetone, and chloroform, and dissolves in cold concentrated sulphuric acid, giving a brilliant azure-blue solution.

122. "*The Action of certain Acidic Oxides on Salts of Hydroxy-acids.* (Part II.). By G. G. Henderson, D.Sc., M.A., and David Prentice.

The action of antimonious and arsenious oxides upon salts of citric, malic, lactic, and mucic acids has been studied, and several new salts have been prepared, the oxide being heated with solutions of salts of those acids for varying periods, and the compounds formed precipitated by alcohol or separated by crystallisation.

With citrates of potassium, sodium, and ammonium, antimonious oxide gave compounds of the general formula $SbOM'_3(C_6H_6O_7)_2 \cdot xH_2O$, which are all crystalline and readily soluble in water. A sparingly soluble barium salt, $SbOBa_3(C_6H_6O_7)_3 \cdot 10H_2O$, was obtained by precipitation, and from it a very soluble crystalline compound of the probable formula $OH \cdot Sb : (C_6H_7O_7)_2$ was prepared. Arsenious oxide gave similar compounds with citrates of the alkalis. They have the general formula—

$$AsOM'_3(C_6H_6O_7)_2 \cdot xH_2O,$$

are crystalline, and dissolve freely in water.

Both antimonious and arsenious oxides dissolve in boiling aqueous solutions of alkaline malates. A well-crystallised antimony compound, whose simplest formula is $(SbO)_3K_4H(C_4H_5O_5)_6 \cdot 3H_2O$, was prepared, but no corresponding arsenic compounds have yet been obtained, owing to their instability.

Boiling solutions of lactates of the alkalis and of barium readily dissolve both antimonious and arsenious oxides, and alcohol precipitates colourless syrups, containing large quantities of unaltered lactates.

Compounds of the oxides with mucates were also prepared, though with some difficulty. Two antimony compounds of the formulæ—

$$2SbOKC_6H_8O_8 \cdot KC_6H_9O_8 \cdot 6H_2O \text{ and } SbOKC_6H_8O_8 \cdot 4H_2O$$

were obtained in the form of sparingly soluble crystalline powders. An arsenic compound corresponding to the second of these was likewise obtained.

These substances might be regarded as double citrates, malates, &c., containing the radicles $(SbO)'$ and $(AsO)'$, but, if so, then in all probability those radicles replace the hydrogen of alcoholic hydroxyl groups, and not the hydrogen of carboxyl groups as in the formation of salts, for otherwise it is difficult to undertsand why hydroxy-acids alone seem to have the power of forming such compounds. On the other hand, they might be regarded as salts of acids derived from antimonious or arsenious acids by replacement of two of the hydroxyl groups of those acids by organic acid radicles, as is the case with the antimonio- and arsenio-tartrates. The formulæ of such acids would be, for antimonio-citric acid—

$$OH \cdot Sb : (C_6H_7O_7)_2,$$

for antimonio-malic acid $OH \cdot Sb : (C_4H_5O_5)_2$, for antimonio-mucic acid $OH \cdot Sb : C_6H_8O_8$; the formulæ of the arsenious acid derivatives would be similar to these. In the case of some at least of the new compounds this view appears preferable.

123. "*Sodium Nitrososulphate.*" By E. Divers F.R.S., and T. Haga.

Sodium nitrososulphate, being a very soluble salt, does not crystallise out when even the strongest solution of sodium sulphite is treated with nitric oxide. But if the solution, after this treatment has been continued long enough, be deprived of most of its sodium sulphate by freezing out, and be then evaporated in a vacuum to a very small volume, sodium nitrososulphate is deposited in crystals.

It is an anhydrous salt, forming very minute crystals, which in the solution adhere together in opaque crusts. The salt is slightly alkaline to litmus, and tastes very much like common salt. It is exceedingly soluble in water and very unstable, wet or dry. In the dry state, in which it can be obtained in a desiccator, and at the common temperature, it rapidly decomposes on exposure to (damp) air, becomes nearly as hot as slaking lime, and gives off large quantities of nitrous and nitric oxides. The residue consists of sodium sulphate and sulphite. It thus behaves at the common temperature as potassium nitrososulphate only does when heated to about 100°.

In solution in water it continuously decomposes, like the potassium salt, into sulphate and nitrous oxide. A little sodium hydroxide greatly retards this decomposition in water, but if a solution of the salt containing sodium hydroxide is heated to boiling, the salt decomposes freely into nitric oxide and sulphite. This behaviour is unlike that of the potassium salt.

Its composition, which was indirectly determined quantitatively, is $Na \cdot ON{:}NO \cdot SO_3Na$.

124. "*The Constitution of Nitrososulphates.*" By E. Divers, F.R.S., and T. Haga.

Potassium nitrososulphate in aqueous solution becomes strongly alkaline when mixed with a little alcohol. This is due to the salt and the alcohol partly decomposing into potassium ethyl sulphate, nitrous oxide, and potassium hydroxide. The primary reaction is, beyond a doubt, one in which potassium hydrogen hyponitrite is produced, along with the potassium ethyl sulphate, although none can be detected; but then its formation proceeds here very slowly, and certainly not faster than it is known to decompose of itself into potassium hydroxide and nitrous oxide.

This reaction is peculiarly interesting, for in it alcohol decomposes a sulphate in alkaline solution, and liberates potassium hydroxide, though indirectly. The occurrence of this reaction, taken with other properties, solves the problem of the constitution of the nitrososulphates. They are anhydro-double salts of hyponitrous and sulphuric acids, which hydrolyse into the acid salts of these acids, the acid salts simultaneously changing into normal sulphate, nitrous oxide, and water. They are analogous to the thiosulphates, the hyponitrite radicle acting as sulphur does in them. Thus we see calcium thiosulphate and sodium nitrososulphate forming themselves from the sulphite of their metal and decomposing into it again, under precisely similar conditions. Nitrososulphates are, however, true sulphates, as their reactions with alcohol and with acidified barium chloride show, their nitrogen being united to their sulphur only though an atom of oxygen, $KON_2 \cdot O \cdot SO_3K$.

(To be continued).

PHYSICAL SOCIETY.

Special Meeting, November 22nd, 1895.

Captain W. de W. Abney, President, in the Chair.

The following resolution with reference to the Articles of Association was passed :—

> "In Article 33 to strike out the words 'by the payment of £10 in one sum,' and in place of this to insert the words 'the composition fee shall be for every member who shall not have paid ten annual subscriptions, fifteen times the amount of the annual subscription payable by such member; and for any member who shall have already paid ten or more annual subscriptions, ten times the amount of the annual subscription payable by such member.'"

The Ordinary Meeting then took place.

Dr. G. Johnstone Stoney exhibited a Print of Profs. Runge and Paschen's Photograph of the Spectrum of the Gas obtained from Clèveite, together with a Diagram illustrating the Manner in which these Observers have arranged *all* the Lines obtained in two Sets, each Set containing Three Series of Lines.

Dr. Stoney also drew attention to the resemblance between each of these sets of three series of lines and the similar triple series obtained in the case of the metals of Mendeleeff's first group. The lines of the different series in the case of the gas obtained from clèveite have certain definite peculiarities, which permit of their identification and selection. The two gases, to the presence of which the two sets of lines are presumably due, can be partly separated by diffusion through a plug of asbestos. Prof. Ramsay's observation that by suitably altering the pressure of the gas the predominance of the lines in either of the two sets can be increased is, however, against the theory that the two gases are really separated by diffusion.

Three of the original negatives taken by Prof. Rowland when preparing his map of the solar spectrum were also exhibited.

Dr. Gladstone said he had examined the spectrum of the gas in two tubes, one of which had been filled by diffusion through an asbestos plug, and the helium line (D_3) was certainly brighter in one tube than in the other, though the brightness of the remaining lines appeared about the same in both tubes. As to the difficulty of allocating the new gases in Mendeleeff's table, it appeared to him (Dr. Gladstone) that they would have to be put in the first group, between hydrogen and lithium. An examination of the successive differences between adjacent members of the metals in the first group showed that these differences increased as we go downward. If, then, the new gases have atomic weights of, say, 2 and 4, we should have for these differences 2, 2, 3, 16, 16, 26, &c., instead of 6, 16, 16, &c., as at present. The important point which required investigation was whether these two gases were really simple bodies or not.

Prof. Silvanus Thompson asked if Runge and Paschen had performed a similar analysis of the lines in the spectra of other elements besides the members of the first group. He would also like to know if, in the case of any element besides hydrogen, the lines could be arranged in a single series.

Dr. Stoney, in reply, said that the spectra of most of the metals had been analysed; the chief exceptions being iron, nickel, cobalt, and manganese. There was no other element besides hydrogen which gave a single series of lines.

Prof. Herschel gave an account of a line of reasoning which had led him many years ago to a formula resembling that expressing Balmer's law for the hydrogen lines, namely,—

$$\frac{1}{\lambda} = 1 - \frac{4}{n^2}\ .$$

The Chairman (Captain Abney) drew attention to the fact that Runge expressed his results to $\frac{1}{1000}$th of an Angström unit, although Dr. Stoney had said the measurements could only be made to within $\frac{1}{50}$th of a unit. There was great lack of uniformity in the method of drawing spectra in general use; he strongly recommended the placing of the red end of the spectrum to the right, so that the wave-lengths increased from left to right. As to the three series of lines obtained in the case of most elements, it was not conclusively proved that they were not due in each case to three distinct kinds of molecules, and it will probably be found that there are more than two simple gases present in the gas evolved from clèveite.

Mr. R. Appleyard read a "*Note on the Action of Sulphur Vapour on Copper.*"

When a copper wire is exposed for some time to the action of sulphur vapour it becomes entirely converted to sulphide of copper, and it is found that there is a fine axial hole running down the rod of sulphide formed. Rods of copper of square section, cut from a block of copper after exposure to the action of sulphur vapour, also exhibited the axial hole, the rod of sulphide formed being of circular cross-section. In every case the diameter of the rod of sulphide formed is about twice that of the original rod of copper. Delta metal was found to be unacted upon by the sulphur vapour.

Mr. Appleyard then read a paper on "*A 'Direct-reading' Platinum Thermometer.*"

This form of platinum thermometer has been devised with the view of determining the temperature of the dielectrics employed in some experiments on the variation of the electrical resistance of dielectrics with temperature. The thermometers consist of six platinum coils, each of about 7 ohms resistance, attached to thick copper leads. A slide-wire Wheatstone's bridge is employed to measure the resistance. The stretched wire is 3 metres long, and the moving contact so arranged that it is impossible to damage the wire. The auxiliary coils used in connection with the bridge are immersed in a bath of paraffin oil, the temperature of which is maintained constant, and a little above that of the air, by means of a glow-lamp immersed in the oil.

Mr. Appleyard also read "*A Historical Note on Resistance and its Change with Temperature.*"

He showed that the earliest measurements of the variation of resistance with temperature were made by Lentz in 1833. Some experiments on this subject made by Davy were also referred to, and some of these experiments repeated before the Society.

Mr. Trotter said he agreed with the author that the "reserve of precision" at our disposal, on account of the delicacy of some of our modern instruments, ought to be made use of to facilitate the rapid performance of many measurements where the utmost accuracy is not necessary. He had the impression that platinum silver was not now considered the best material for use as the bridge wire.

Mr. H. F. Burstall explained the differences between the temperature as measured on the mercury, air, and platinum thermometers. At a temperature of about 40° the platinum thermometer read about 0·4°, and the mercury thermometer about 0·1° below the air thermometer. Prof. Callendar had obtained measurements of temperature correct to within 0·1° by using a Weston voltmeter and an ordinary Wheatstone bridge; the variations of resistance, and hence the temperature, being read directly from the deflections on the voltmeter.

Mr. Rhodes thought that, except where extreme accuracy was necessary, the mercury thermometer was very much more convenient than the platinum thermometer.

Mr. Burstall said the great convenience of the platinum thermometer lay in the fact that the scale could be read at a distance of many yards from the point where the temperature was being measured, and hence could be used in many places where it would be impossible to read a mercury thermometer.

Mr. Blakesley considered that the author was somewhat bold to state that for general purposes it was never necessary to measure temperature to nearer than one-tenth of a degree.

The author having replied, the Society adjourned till December 13th.

Appointment.—Mr. W. Lincolne Sutton, A.I.C., has been appointed Public Analyst for the city of Norwich.

Pasteur's Successors. — According to the *Chemiker Zeitung* a dispute has arisen in the Pasteur Institute as to the succession to the presidency of this establishment, Duclaux or Roux. Duclaux ranks high in the scientific world, whilst Roux figures as a physician. The Council of the Institute finally decided in favour of Duclaux, whilst Roux is appointed Second Director. It is not generally known that Pasteur, in addition to his scientific eminence, was distinguished as a financier.

NOTICES OF BOOKS.

A Treatise on the Manufacture of Soap and Candles, Lubricants, and Glycerin. By Wm. Lant Carpenter, B.A., B.Sc., F.C.S., &c. Second Edition, Revised and Enlarged by Henry Leask. London: E. and F. N. Spon. New York: Spon and Chamberlain. 1895. Crown 8vo., pp. 446.

It is satisfactory to find that this work has not undergone any deterioration from the regretted death of its author. The second edition, now before us, has been entrusted to Mr. Henry Leask, a recognised authority on paraffin refining and on the manufacture of candles.

In the first chapter we are rightly told that though soap was in use prior to the Christian Era, yet the modern development of the soap manufacture dates only from the early part of the present century, and is substantially due to two French inventors, Chevreul and Leblanc.

We regret the recent decline in the consumption of palm-oil, since in vegetable fats we are substantially safe from the presence of the morbid products of microscopic life. The author refers to the liability of cocoanut-oil and palm-oil to turn rancid. We once knew of a cask of the latter oil reaching the consumer, in Yorkshire, perfectly free from rancidity. This was practically no advantage, since the greater part was eaten by the workmen. Concerning linseed oil, the author mentions a fraud practised in the Russian ports, viz., the addition of 1 measure of hemp seed to every 39, or latterly 19, measures of linseed. In India the oil seeds are often grown promiscuously. Indeed to obtain absolutely pure oils for any scientific purpose is a difficult and doubtful matter.

The vegetable tallows, the products of species of *Hopea*, and of *Stillingia salifera*, are found, as lubricants, superior even to olive oil.

The following remark is gravely significant:—"The soap-pan appears to be the natural destination of any rough fat-containing matter which can be turned to no other purpose."

It is interesting that large quantities of Fuller's earth are yet exported from this country to America to serve in the purification of lard. The bleaching of oils and fats still offers scope to the inventor, since many agents which decolourise at the same time promote rancidity.

The problem of recovering glycerin from spent lyes is rightly pronounced very difficult, and it is regarded as probable that in the future all glycerin will be obtained directly from fats prior to saponification.

The difficulty of correct sampling solid and semi-solid fats is insisted upon. The identification of oils in mixtures—and there are few samples which may not be regarded as mixtures—is discussed at some length. The spectroscope assists us only in some cases. Maumené's test, according to Allen, sometimes gives unaccountable results.

When soap-makers manufacture their own alkali, their operations are much complicated, and require more plant and space; hence whether such causticising is economical or not must depend on local conditions. The Solvay alkali process will not, it is considered, commend itself to the adoption of soap-boilers, though the ammonia-soda is excellent. It is to be regretted that in the English alkali trade the false atomic weight 24 is still used instead of 23, the correct figure. We may here regret the countenance given to Baumé's hydrometer in this work, though two pages are given up to its inconsistencies (pp. 278 and 279).

The common opinion that a soap-work is necessarily a public nuisance is totally erroneous. Such an establishment, if well-conducted, is far less offensive than, *e.g.*, a fried-fish shop.

Space will not allow us to extend our notice of this book to the remaining portions, which treat of lubricants and of the manufacture of candles. Upon the whole, this second edition may be regarded as an improvement upon its predecessor. It will be found a useful manual by the student of those departments of technical chemistry which discuss the applications of the oils and fats.

Perken, Son, and Rayment's Illustrated Catalogue of Photographic Apparatus, Magic Lanterns, and Optical Instruments: contains numerous Reductions in Prices, many Novelties, and Fresh Matter. "Optimus," 99, Hatton Garden, Holborn Viaduct, and 141, Oxford Street, W., London.

The photographer, be he professional or amateur, will find here ample scope for choice of cameras and all other fittings and accessories. The lanterns shown are a great convenience for scientific lecturers, as well as for their hearers.

The old "sketching lecture," in which an awkward representation of apparatus, of specimens, or dissections, was given by dint of chalk and black-board, is evidently and deservedly fading into the "infinite azure," whilst the lecturer can, by means of the lantern and of appropriate slides, give a far clearer and more accurate view of the objects to be explained.

The catalogue before us gives a wonderful assortment of slides, suitable for illustrating all kinds of lectures, astronomical, historical, geological, antiquarian, biological, and miscellaneous.

In this catalogue, as we believe in all others issued by opticians, we notice that the spectroscope does not figure prominently, if at all. This is a proof that an instrument so necessary for research in various sciences is very rarely, as yet, in demand by investigators.

CORRESPONDENCE.

PRODUCTION OF CITRIC ACID BY THE OXIDATION OF CANE-SUGAR.

To the Editor of the Chemical News.

Sir,—We certainly "profess to have repeated" Dr. Phipson's experiments, and have taken care to follow his instructions implicitly. We fail to see why he should state that we have not done so.

Dr. Phipson now says that the products of oxidation of cane-sugar by permanganate vary considerably, "according to the respective quantities of permanganic acid and sugar, according as sulphuric acid or nitric acid is used, and according to the temperature of the day." We have employed the reagents in the proportions Dr. Phipson recommended, and have failed to produce any citric acid, as we also did on previous occasions when we used our own discretion as to the proportions of the materials.

If Dr. Phipson will tell us any better way of recognising citric acid in a liquid also containing tartaric acid, saccharic acid, and formic acid, than that based on the precipitation of calcium citrate by boiling a neutral solution, we shall be glad to try his process. We confess that we do not know any better plan.

Dr. Phipson, in conclusion, asks us what becomes of the sugar, if saccharic acid, tartaric acid, formic acid, and citric acid are not formed. Saccharic acid is well known to be a product of the oxidation of cane-sugar, and tartaric acid, we have reason to believe, can be obtained under suitable conditions. The question of formic acid is open. It is for Dr. Phipson to prove that citric acid is formed, as asserted by him, and to prescribe a method by which other chemists can repeat his experiments successfully.—We are, &c.,

Alfred B. Searle,
Arnold R. Tankard.

67, Surrey Street, Sheffield,
November 23, 1895.

CHEMICAL EDUCATION.

To the Editor of the Chemical News.

Sir,—In your "Address to Students" in the number last to hand (Chemical News, vol. lxxii., p. 111), you refer to the chemical education obtainable and appreciated, and therefore paid for, in Germany. I have seen the same matter often written of for some years, and the want of progress in chemical industries in Great Britain ascribed to the want of appreciation of such trained skill, by British manufacturers. It is always advantageous to trace things to their first cause; and I think that in this case it may be found in a remark made to me in the early sixties by Dr. E. Ronalds, then in Edinburgh. I had formerly been his assistant, he being managing partner in the Bonnington Chemical Works, where the tar from Edinburgh and Leith was treated, and I made some mauve from aniline in a fractionated series of coal-tar bases shortly after Perkins patented his process—about 1857, I think—and on the occasion referred to, whilst speaking of the coal-tar colours, he said:—"The Excise will drive the business out of the country, so there is no use touching it."

Actually this is what has happened, as the Government by the duty on alcohol, and the rigorous regulations as to its use, have driven a trade worth £20,000,000 per annum out of Great Britain. For the greater part of the thirty-eight years since the industry began, the greater portion of the raw material was provided by the United Kingdom, and all the first colours were discovered and made there, showing that the chemical knowledge was there. The use of free alcohol then transferred the manufacture to Germany. The manufacturer demanded technical chemists; and technical chemical schools arose, not only supplying the demand, but leaving a surplus of trained men which has overflowed into every branch of chemical industry. And now the supply of the raw material for that manufacture is curtailed to the United Kingdom, in consequence of German improvements in coke making, so that benzine, which used to be 15/- per gallon, is now 1/-.

In the first half of this century the great strides in industrial chemistry were made in bleaching and light production, and that in the United Kingdom; and that as the Government did not interfere with them they took root and flourished. In the second half of the century, the great stride has been in colours; but here the Government insisted on its pound of flesh, so this industry fled, and, in consequence, other British chemical manufactures are threatened.

To support technical schools there must be a demand for those trained in them, and good positions in view; and this can only come from a rapidly growing industry in which a few have drawn prizes and hundreds think they may do the same. Other industries which have arrived at the rule-of-thumb stage are benefited only indirectly, and it must be remembered that what is the highly scientific to-day becomes the rule-of-thumb of a few years hence.—I am, &c.,

W. A. D.

Sydney, October 21, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 19, November 4, 1895.

Action of Silicon upon Iron, Chromium, and Silver.—H. Moissan.—This paper will be inserted in full.

Spectral Researches on the Star Altair (α-Aquilæ).—H. Deslandres.—The bulk of this memoir is purely astronomical, but it may be here mentioned that, unlike the other white stars, Altair has iron and calcium rays almost as broad as the rays of hydrogen. They have been detected on seeking for, among the broad black rays of the spectrum, the small brilliant reversed rays which constitute the bulk of the atmospheric spectrum.

Treatment of the Emerald and the Preparation of Pure Glucina.—P. Lebeau.—This memoir will be inserted in full.

On a Group of Mineral Waters containing Ammonia; Bituminous Waters.—F. Parmentier.—The waters in question are obtained from springs in the neighbourhood of Clermont. Ammonia can be detected in them by means of the Nessler reagent. Beyond bituminous matter, recognisable by the smell and taste, there is no other organic matter.

Determination of Tannin in Wines.—E. Manceau.—The author's method is as follows:—About 100 c.c. of wine are placed in a small flask with a ground glass stopper, and 1 grm. of gut-string. In a week, at about 15°, all the tannin will have been taken up. He then titrates with a solution of permanganate, 1 c.c. of which corresponds to 0·2 m.grm. of pure gallo-tannin, using as indicator a sulphuric solution of indigotin. The difference of the volumes of permanganate taken to decolourise 25 c.c. of the original wine and 25 c.c. of the same wine deprived of tannin shows the weight of gallotannin corresponding to 25 c.c. of the wine. To prepare the gut-strings, violin strings (not oiled) are submitted in succession to prolonged washing in alcoholised water, acidulated water, and pure water, until they no longer yielded to these solvents any substance capable of reducing permanganate in the cold.

Action of Chlorine upon Normal Propylic Alcohol.—André Brochet.—The author has made an especial study of α-chloropropionic aldehyd and of chlorodipropylicpropional.

Ozotoluene.—Adolphe Renard.—If pure toluene is submitted to the action of ozone, there is formed an explosive product, ozotoluene, analogous to ozobenzene. It forms a white translucent mass, of a gelatinous aspect. It decomposes at from 8° to 10°. Its composition is probably $C_7H_8O_6$, whence it is the higher homologue of ozobenzene, $C_6H_6O_6$. With pure xylene (ortho-xylene) submitted to ozone at 0° there is also obtained a white explosive product.

Study of the Nitration of Menthone.—M. Konavaloff.—The author has obtained a product of the composition $C_{16}H_{17}(NO_2)O$.

Fermentation of Cellulose.—V. Omelianski.—This phenomenon has generally been ascribed to the action of *Bacillus amylobacter*. This organism the author regards as a "collective species." The pure bacillus he considers to be slender, consisting of straight and sinuous joints, from 6 to 7 μ in length and 0·2 to 0·3 μ in breadth. It forms regular round spores.

Experiments on the Direct Production of Pure Ethylic Alcohol by the Fermentation of Asphodelus ramosus and Scilla maritima by the Aid of Pure Wine Ferments.—G. Rivière and M. Bailhache.—The nature of this paper appears sufficiently from the title.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 117.

The Expansion of Glass, and on Soldered Glasses.—A Report presented by Dr. Schott.—For siliceous glasses the expansion increases with the proportion of alkali. Boric acid produces a striking decrease of expansion. In superposing upon each other two glasses of different compositions, it is requisite that there should exist a certain relation between the relative thickness of the two layers of glass and their coefficients of expansion. Thus at Jena they solder normal thermometer glass, the coefficient of cubic expansion of which between 0° and 100° = 0·0000244, to an aluminous sodium borosilicate the expansion of which = 0·0000177. The former kind of glass must be placed externally and the second internally in order to form a hollow vessel or a tube. We may also join together three or more layers of two or more glasses. Of two layers of glass with different expansions, after cooling, that with the greatest expansion will be in a state of tension, and the other in a state of compression. External layers in a state of compression increase in a striking manner the resistance of glass to mechanical actions and to rapid changes of temperature. Flasks thus manufactured may be strongly heated (to a temperature of 184°), and may then be sprinkled with cold water without injury. Such glasses are not liable to the sudden rupture presented by glass tempered by the process of De la Bastie.

MEETINGS FOR THE WEEK.

Monday, 2nd.—Society of Arts, 8. "Mechanical Road Carriages," by H. Worby Beaumont, M. Inst.C.E. (Cantor Lectures).

— Society of Chemical Industry, 8. "Alkali Manufacture by the Hargreaves Bird System of Electrolysis," by Mr. J. Hargreaves, F.C.S. "The Analysis of Chrome Iron Ore, Ferrichrome, and Chrome Steel," by Dr. S. Rideal and Mr. S. Rosenblum.

— Royal Institution, 5. General Monthly Meeting.

Wednesday, 4th.—Society of Arts, 8. "Mural Painting, with the Aid of Metallic Oxides and Soluble Silicates," by Mrs. Anna Lea-Merritt and Prof. W. C. Roberts-Austen, C.B., F.R.S.

Thursday, 5th.—Chemical, 8. "The Constitution of Terpenes," by Prof. Armstrong, F.R.S. "New Derivatives from α-Dibromo-camphor," by M. O. Forster. "The Chemistry of Dibromopropylthiocarbimide, and the Action of Bromine and Iodine on Allylthiourea," by Prof. A. E. Dixon. Ballot for the Election of Fellows.

THE CHEMICAL NEWS.

Vol. LXXII., No. 1880.

ON THE
NEW GASES OBTAINED FROM URANINITE.*
(Sixth Note).

By J. NORMAN LOCKYER, C.B., F.R.S.

As Mr. Crookes has now published (Chemical News, vol. lxxii., p. 87) the wave-lengths of the lines in the spectra of the new mineral gases observed by him in the tubes supplied by Professor Ramsay, I propose in the present paper to bring together some notes I have made (some of them some time ago) on the same subject.

The researches made at Kensington in connection with the new gases obtained from bröggerite and other minerals has consisted, to a large extent, of comparisons of the lines in their spectra with lines in the spectra of the sun and stars. Preliminary accounts of these comparisons have already been given, and they show that the bright yellow line seen in the gas from bröggerite is by no means the only important one which appears.

Although the general distribution and intensities of the lines in the gases from bröggerite and clèveite sufficiently corresponded with some of the chief "unknown lines" in the solar chromosphere and some of the stars to render identity probable, it was desirable to see how far the conclusion is sustained by detailed investigations of the wave-lengths of the various lines.

The Yellow Line λ 5875·9.—Immediately on receiving from Professor Ramsay, on March 28th, a small bulb of the gas obtained from clèveite, a provisional determination of wave-length was made by Mr. Fowler and myself, in the absence of the sun, by micrometric comparisons with the D lines of sodium, the resulting wave-length being 5876·07 on Rowland's scale. It was at once apparent, therefore, that the gas line was not far removed from the chromospheric D_3, the wave-length of which is given by Rowland as 5875·98.

The bulb being too much blackened by sparking to give sufficient luminosity for further measurements, I set about preparing some of the gas for myself by heating bröggerite *in vacuo*, in the manner I have already described. A new measurement was thus secured on March 30 with a spectroscope having a dense Jena glass prism of 60°; this gave the wave-length 5876·0.

On April 5th, I attempted to make a direct comparison with the chromospheric line, but though the lines were shown to be excessively near to each other, the observations were not regarded as final.

Professor Ramsay having been kind enough to furnish me, on May 1, with a vacuum tube which showed the yellow line very brilliantly, a further comparison with the chromosphere was made on May 4. The observations were made by Mr. Fowler, in the third order spectrum of a grating having 14438 lines to the inch, and the observing telescope was fitted with a high-power micrometer eye-piece; the dispersion was sufficient to easily show the difference of position of the D_3 line on the east and west limbs, due to the sun's rotation. Observations of the chromosphere were therefore confined to the poles.

During the short time that the tube retained its great brilliancy, a faint line, a little less refrangible than the bright yellow one, and making a close double with it, was readily seen, but afterwards a sudden change took place, and the lines almost faded away. While the gas line was brilliant, it was found to be "the least trace more refrangible than D_3, about the thickness of the line itself, which was but narrow" (Observatory Note-book"). The sudden diminution in the brightness of the lines made subsequent observations less certain, but the instrumental conditions being slightly varied, it was thought that the gas line was probably less refrangible than the D_3 line by about the same amount that the first observation showed it to be more refrangible. Giving the observations equal weight, the gas line would thus appear to be probably coincident with the middle of the chromospheric line, but if extra weight be given to the first observation, made under much more favourable conditions, the gas line would be slightly more refrangible than the middle of the chromosphere line.

Pressure of other work did not permit the continuation of the comparisons. In the meantime, Runge and Paschen announced (*Nature*, vol. lii., p. 128) that they also had seen the yellow line of the clèveite gas to be a close double, neither component having exactly the same wave-length as D_3, according to Rowland.

They give the wave-length of the brightest component as 5878·883, and the distance apart of the lines as 0·323.

This independent confirmation of the duplicity of the gas line led me to carefully re-observe the D_3 line in the chromosphere for evidences of doubling. On June 14, observations were made by Mr. Shackleton and myself of the D_3 line in the 3rd and 4th order spectra under favourable conditions; "the line was seen best in the 4th order, on an extension of the chromosphere or prominence on the north-east limb of the sun. The D_3 line was seen very well, having every appearance of being double, with a faint component on the red side, dimming away gradually; the line of demarcation between the components was not well marked, but it was seen better in the prominence than anywhere else on the limb." ("Observatory Note-book").

It became clear, then, that the middle of the chromosphere line, as ordinarily seen, and as taken in the comparison of May 4, does not represent the place of the brightest component of the double line, so that exact coincidence was not to be expected.

Though the observations are not yet quite completed, the circumstance that the line is double in both gas and chromosphere spectrum, in each the less refrangible component being the fainter, taken in conjunction with the direct comparisons which have been made, render it highly probable that one of the gases obtained from clèveite is identical with that which produces the D_3 line in the spectrum of the chromosphere.

Other observers have since succeeded in resolving the chromospheric line. On June 20, Professor Hale found the line to be clearly double in the spectrum of a prominence, the less refrangible component being the fainter, and the distance apart of the lines being measured as 0·357 tenth-metres (*Ast. Nach.*, 3302).

The doubling was noted with much less distinctness in the spectrum of the chromosphere itself on June 24. Professor Hale points out that Rowland's value of the wave-length (as well as that of 5875·924, determined by himself on June 19 and 20) does not take account of the fact that the line is a close double.

Dr. Huggins, after some failures, observed the D_3 line to be double on July 10 (*Ast. Nach.*, 3302); he also notes that the less refrangible component was the fainter, and that the distance apart of the lines was about the same as that of the lines in the gas from clèveite, according to Runge and Paschen.

It may be added, that in addition to appearing in the chromosphere, the D_3 line has been observed as a bright line in nebulæ by Dr. Copeland, Professor Keeler, and others; in β Lyræ and other bright line stars; and as a dark line in such stars as Bellatrix, by Mr. Fowler, Professor Campbell, and Professor Keeler. In all these cases it is associated with other lines, which, as I shall show presently, are associated with it in the spectra of the new gases.

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* A Paper read before the Royal Society, November 21, 1895.

Wave-length (Rowland).	Wave-length (Angström),	Chromosphere (Young).	Eclipses 1893. Max. intens.=10.	Orion nebula. Max. intens.=6.	Bellatrix. Max. intens.=6.	Crookes's measures.
		Frequency.	λ R.	λ R.	λ R.	λ R.
7065·5	7064·0	100	..	..	..	7065·5
6678·3	6676·9	25	..	..	..	6678·1
6371·6	6370·5	5				
6347·3	6346·2	10				
6141·9	6140·6	15				
6122·43	6121·43	5				
6065·7	6064·5	5				
5991·6	5990·0	15				
5875·9	5874·9	100	5876·0	5876·0	5876·0	5876·0
5429·9	5428·8	8				
5404·1	5403·1	5				
5048·2	5047·8	2	..	..	..	5047·1
5015·8	5015·0	30	5016·0(4)	..	5016·0(1)	5015·9
4922·3	4921·3	30	4922·0(4)	4924(3)	4922·0(2)	4922·6
4713·4	4712·5	2	4713·2(5)	4716(2)	4715·0(3)	4713·4
4471·8	4471·2	100	4471·8(10)	4472(4)	4472·0(6)	4471·5
4389·5	4388·5	1	4390·0(1)	4390(2)	4389·0(5)	4386·3
4026·5	4025·9	*	4026·0(6)	4026(3)	4026·0(6)	4026·1
3964·0	3963·5	—	3963·8	..	3964·0(3)	3964·8
3888·7	3888·0	—	probable†	..	probable	3888·5

* Professor Young has recently called attention to the fact that although this line was not included in his chromospheric list, he observed and published it in 1883; its frequency is about 15. (*Nature*, vol. lii., p. 458).

† This line is too close to a hydrogen line to enable a definite statement to be made.

The Blue Line, λ 4471·8.—A provisional determination on April 2 of the wave-length of a bright blue line, seen in the spectrum of the gases obtained from a specimen of clèveite, showed that it approximated very closely to a chromospheric line, the frequency of which is stated as 100 by Young.

This line was also seen very brilliantly in the tube supplied to me by Professor Ramsay on May 1, and on May 6 it was compared directly with the chromosphere line by Mr. Fowler. The second order grating spectrum was employed. The observations in this region were not so easy as in the case of D_3, but with the dispersion employed, the gas line was found to be coincident with the chromospheric one. In this case also, the chromosphere was observed at the sun's poles, in order to eliminate the effects due to the sun's rotation.

In a former note (*Roy. Soc. Proc.*, vol. lviii., p. 114), I have pointed out that this line does not appear in the spectra of the gases obtained from all minerals which give the yellow line.

Besides appearing in the spectrum of the chromosphere, the line in question is one of the first importance in the spectra of nebulæ, bright line stars, and of the white stars such as Bellatrix and Rigel.

The Infra-red Line, λ 7065·5.—In addition to D_3, and the line at 4471·8, there is a chromospheric line in the infra-red which also has a frequency of 100, according to Young. On May 28, I communicated a note to the Royal Society stating that this line had been observed in the spectrum of the gases obtained from bröggerite and euxenite (*Roy. Soc. Proc.*, vol. lviii.), solar comparisons having convinced me that the wave-length of the gas line corresponded with that given by Young; and I added "it follows, therefore, that besides the hydrogen lines, all three chromospheric lines in Young's list which have a frequency of 100 have now been recorded in the spectra of the new gas or gases obtained from minerals by the distillation method."

M. Deslandres, of the Paris Observatory, has also observed the line at 7065 in the gas obtained from clèveite (*Comptes Rendus*, June 17, 1895, p. 1331).

Other Lines.—Determinations of the wave-lengths of many other lines in the spectra of the new gases have been made, chiefly with the aid of a Steinheil spectroscope having four prisms, and the results leave little doubt as to the coincidence of several lines with those appearing in the chromosphere, nebulæ, and white stars.

It seems very probable, also, that many lines which have been noted, and for which no origins have yet been traced, belong to gases which have not hitherto been recorded in the chromosphere.

The accompanying table summarises the chief lines which have so far been recorded in the new gases from various minerals, some of which show D_3 while others do not. Only those lines which also appear in the spectrum of the chromosphere, nebulæ, or Orion stars, are given in the first instance. There are other lines which are probably also associated with chromospheric ones, but further investigation of them is considered desirable before they are included in the list.

The first column of the table gives the wave-lengths of the lines on Rowland's scale, while the second gives the wave-lengths on Angström's scale; the third gives the frequency of the lines in the chromosphere according to Young. In the fourth column lines photographed with the prismatic camera during the total eclipse of April 16, 1893, are shown; these have been included because in some cases lines which appear to be comparatively unimportant in Young's list were photographed as important lines. The fifth column indicates probable coincidences with lines in the spectrum of the Orion nebula; the accuracy of these wave-lengths is of necessity less than in the case of the chromosphere; with the exception of D_3 they are taken from my paper on the photographic spectrum of the Orion nebula (*Phil. Trans.*, 1895, vol. clxxxvi. A, p. 76). The sixth column shows probable coincidences with dark lines in the spectrum of Bellatrix, this being taken as an example of the Orion stars (*Phil. Trans.*, 1893, vol. clxxxiv. A, p. 695), the lines 4922·3 and 5015·8 have been photographed since the date of the paper to which reference is made.

The last column gives the wave lengths, from Mr. Crookes's table, of the lines observed by both of us.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on December 2nd, Sir James Crichton-Browne presiding. The following were elected Members:—Messrs. C. H. Berners, J.P., J. M. Bruce, M.D., F. Chambers, A. M. Chance, J.P., A. E. Fletcher, F. Fox, J.P., H. Seymour, K. T. Stewart, M.D., G. H. Strutt, F. Tendron, F.G.S., W. H. Warner, M. Webb, J.P., and Mrs. S. H. Phillips.

EXPERIMENTAL PROOF OF VAN 'T HOFF'S CONSTANT, OF ARRHENIUS'S GENERALISATION, OF OSTWALD'S LAW OF DILUTION, OF DALTON'S LAW, &c., IN VERY DILUTE SOLUTIONS.*

By Dr. MEYER WILDERMANN.

The following forms the foundation of the new theory of solutions:—

1.—*Proof of van 't Hoff's Constant.*

It was van 't Hoff who first drew attention to the fact that the equations representing the generalisations arrived at by Boyle, Gay-Lussac, and Avogadro in the case of gases are equally applicable to dissolved substances, if the osmotic pressure of the molecules of the dissolved substance be substituted for the pressure of the gas. Van 't Hoff deduced these laws for solutions from thermodynamical considerations (*Zeit. Phys. Chem.*, i., 1887)—a method which gives them increased validity—and illustrated them from the osmotic experiments of Pfeffer and de Vries. Soon after, Prof. Max Planck deduced van 't Hoff's laws in a very elegant way, also from thermodynamical considerations (*Wied. Ann.*, xxxii., 1887). Lorentz (*Zeit. Phys. Chem.*, vii.), Boltzmann (*Zeit. Phys. Chem.*, vi., vii.), Riecke (*Zeit. Phys. Chem.*, vi.), and Van der Vaals (*Zeit. Phys. Chem.*, v.) have deduced the gaseous laws from the kinetic theory.

At the same time van 't Hoff was able to establish a thermodynamical relation between the osmotic pressure of a dissolved substance and the molecular lowering of freezing-point of the solution, thereby furnishing a rational basis for the empirical generalisations of Raoul, Babo, and Wüllner, who had previously investigated the same point (*Zeit. Phys. Chem.*, i.); later on Planck deduced the same thermodynamical relations (*Wied. Ann.*, xxxii., 1887).

In van 't Hoff's thermodynamical argument the solutions are assumed to be very dilute, and hence their experimental verification is of special importance in very dilute solutions. The determination of the molecular freezing-point is the safest and the most convenient method of testing the validity of these generalisations experimentally, and this has been done for moderately dilute solutions by van 't Hoff himself, and by Eykmann, and the equation—

$$t = \frac{0{\cdot}02\,T^2}{w};$$

where T = absolute temperature, w = latent heat of fusion of the solvent, has been experimentally verified and confirmed for several solvents. The method of determining the freezing-point in very dilute solutions of my late friend P. B. Lewis (*Trans. Chem. Soc.*, 1894; a fuller account has been given in *Zeit. Phys. Chem.*, xv., p. 358), my investigations on the same matter ("On the Determination of the Freezing-point of Water," *Zeit. Phys. Chem.*, xv., p. 365. See "On the Real and Apparent Freezing-points and the Freezing-point Methods," then "On the Determination of Freezing-point in Dilute Solutions to 0·4° Depression," which I shall publish shortly in *Phil. Mag.* and in *Zeit. Phys. Chem.*) give us the possibility of submitting van 't Hoff's equation,—

$$t = \frac{0{\cdot}02\,T^2}{w},$$

to a more accurate verification. I give a full account of the freezing-point method, since it is important to know not only what one gets, but how it is got. This is especially necessary in view of the different contradictory results which have been published and are due to insufficient, and often more than insufficient, development of the method used. Last year I investigated a series of bodies (*Phil. Mag.*, July, 1895); this year I investigated cane-sugar, urea, alcohol, dextrose, resorcin, maltose, milk-sugar, glycerin, with the convergence temperature above and below the freezing temperature, with the $\frac{1}{1000}$° and the $\frac{1}{100}$° thermometer, with different parts of the scale. The obtained results are in excellent agreement with van 't Hoff's theory.

2.—*Arrhenius's Generalisation.*

Van 't Hoff showed, by four different methods, that a generalisation analogous to that of Avogadro was valid for solutions of non-electrolytes, like cane-sugar; it then became of importance to account for exceptional cases, in which the depression of the freezing-point was abnormal, and in particular the cases of salts, acids, and bases in aqueous solutions. The explanation was given when Arrhenius showed that, by two independent, quite different, methods, the observation of the lowering of freezing-point and of the electrical conductivity of a solution, the same value would be obtained for the factor i, which denotes the ratio of the pressure actually exerted by the substance to the pressure which the substance would exert if it consisted entirely of undissociated molecules. Arrhenius made determinations on about forty bodies in moderately dilute solutions of various concentrations, and verified his generalisation. From the intimate connection which exists between van 't Hoff's laws and the dissociation theory, it follows also that the generalisation of Arrhenius may find a more exact experimental confirmation in dilute solutions. This is not only important on account of the great light which the theory of dissociation has thrown upon the two provinces of chemistry and physics, but it is also important inasmuch as thereby the laws of van 't Hoff will find in every point their more exact confirmation (see also Max Planck, *Wied. Ann.*, xxxiv.).

Last year I investigated sulphuric acid, potassium chloride, dichloracetic acid, orthonitrobenzoïc acid, trichloracetic acid, with the convergence temperature above the freezing temperature (*Phil. Mag.*, July, 1895); this year, with the convergence temperature below the freezing temperature. Besides these bodies I investigated nitric acid, hydrochloric acid, potassium chloride, sodium chloride, ammonium chloride, &c., with the convergence temperature below the freezing temperature. Arrhenius's generalisation finds the most wonderful confirmation.

3.—*The Law of Dilution.*

This forms one of the most important foundations of the theory of dissociation. It was Ostwald who first showed the relation between the dissociated and undissociated molecules to depend upon the action of masses, and took pains to verify the same in the case of about two hundred acids by means of their electric conductivity (see, also, Max Planck, *Wied. Ann.*, xxxiv.).

From the above-mentioned generalisation of Arrhenius it follows that the law of dilution ought also to be deducible from the freezing-points, since the freezing-points, as well as the electric conductivity, enable us to know the degree of dissociation, and it may be interesting inasmuch as we have not here to do with velocity of ions or with the theory of electric conductivity.

From the intimate connection which exists between van 't Hoff's laws and the theory of dissociation, it follows that the law of dilution must find its experimental confirmation in dilute solutions; the freezing-point methods have not been till now sufficiently exact for this purpose; now we are able to undertake it under favourable conditions.

I investigated orthonitrobenzoïc acid, dichloracetic acid, trichloracetic acid, with the convergence temperature above (*Phil. Mag.* July, 1895) and below the freezing temperature, and found that the law of dilution finds a good confirmation also by this second way.

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* Read before the British Association (Section B), Ipswich Meeting, 1895.

4.—*Dalton's Law in Solutions.*

Dalton's law, as we know, declares that the total pressure of a mixture is equal to the sum of the partial pressures exerted by the constituents of the mixture in the given space. This law, for the same reason as the law of Boyle and Gay-Lussac, holds good only in the case of dilute gases. Since van 't Hoff has shown that the law of Boyle and Gay-Lussac is to be applied for dilute solutions (see van 't Hoff's constant), the conclusion may logically be drawn that the third gaseous law—the law of Dalton—exists in solutions also. For some reasons, which cannot be further discussed here, the best mode of testing Dalton's law in solutions is the freezing-point method. I investigated, for this purpose, mixtures of urea and resorcin, of urea and cane-sugar, of urea and dextrose, of dextrose and cane-sugar; the obtained results, in very dilute solutions (with the convergence temperature under the freezing-point), are very satisfactory—no less than in the case of the proof of van 't Hoff's constant.

5.—*On the Degree of Dissociation in Solutions when Non-electrolytes are present.*

It has been found that the degree of dissociation of a gas does not change in the presence of an indifferent gas. This is also to be regarded as a consequence of Dalton's Law for the partial pressures of the constituents of a mixture. I find the relations to be quite analogous in the case of electrolytic dissociation. I investigated the influence of glycerin upon dichloracetic acid, upon orthonitrobenzoic acid, &c.; the result is, that no change (at any rate no considerable change) in the degree of dissociation takes place, even in the case of dichloracetic acid and orthonitrobenzoic acid. These investigations of the influence of non-electrolytes on the degree of dissociation by the method of freezing-points is of special interest, since, besides the phenomena under consideration, the theory of electric conductivity can be more easily surveyed and understood by this than by using the method of electric conductivity (as has been done by Arrhenius) where the above phenomenon is complicated by the change of the velocity of ions, owing to the change of the inherent viscosity ("innere Reibung") of the liquid. Using the method of freezing-points, we are able to isolate the phenomena and to come to a clear conception of both of them. At any rate no considerable reduction of the degree of dissociation, I find, takes place when non-electrolytes are present, and the diminution of the electric conductivity of a dissolved electrolyte in the presence of a non-electrolyte must, more or less, be entirely attributed to the change of the inherent viscosity.

6.—*On the Reduction of the Degree of Dissociation by introducing a Common Ion.*

I have already drawn attention to the importance of the law of dilution as a proof of the theory of dissociation, which shows that the relation between the dissociated and undissociated molecules depends upon the well-investigated and established law of action of masses. A second proof of the theory of dissociation, based upon the same law of action of masses, is the reduction of the degree of dissociation by the introduction of a common ion. In the case of a dissociated gas, a reduction of the degree of dissociation takes place if one of the dissociated parts is introduced. It was Arrhenius who first, in his paper, "Theory of Isohydric Solutions" (*Zeits. Phys. Chem.*, ii.), drew attention to this important point, as a proof of the theory of dissociation. Arrhenius himself proved this question but little, using the method of electric conductivity. A more searching investigation of this matter by the method of electric conductivity has been undertaken at the same time by Prof. Ostwald in Leipzig, and myself in Oxford. It is important to mention that the agreement between the theory and the obtained results is very satisfactory. Here I give the results which I obtained by the investigation of the same matter in dilute solutions by a second method — the freezing-point method. I investigated the reduction of dissociation in the case of mixtures of hydrogen chloride and orthonitrobenzoic acid, hydrogen chloride and dichloracetic acid, nitric acid and orthonitrobenzoic acid, nitric acid and dichloracetic acid, nitric and hydrochloric acid, &c. I have calculated, owing to want of time, only a part of my experimental results, and, as far as my calculations have been carried out, the agreement between the theory and the experiments is quite satisfactory. I draw attention to the fact that, while non-electrolytes did not produce reduction of dissociation in the case of dichloracetic acid and orthonitrobenzoic acid, we, quite in accordance with the law of action of masses, have been able for the same bodies, by introducing common ions, to observe reductions of dissociation which amount even to 60 or 70 per cent of the total value of the degree of dissociation.

Christ Church, Oxford.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 261).

B. *Air of the Laboratory.*—The laboratory, situated on the second floor, consisted of two rooms, one of which looked on to the street and the other on to the garden. These rooms communicated with each other by a door, and had in addition a door opening on to the landing, which supplied them with air coming from the roof or basement, according as the door of the loft or basement was open or shut.

The apparatus for condensing vapour from the air was freely suspended in the back room, in a very large glass cage, having in its upper part a large opening which could be lessened at will, connected with a ventilating shaft, and receiving air from the room through a large opening 70 c.m. above the floor.

The spectroscope was placed in the same room, 1·5 metres from the condensing apparatus. The front room, the landing-door of which was open, supplied air to the back room.

1st. The wind was blowing from the east, the air came from the yard in the south-west, by the staircase well and the landing. The temperature of the air in the glass cage was 22·5°; dew-point was 15·2°. The weight of water condensed was 132 grms. During the period of condensation of water vapour, the temperature of the disulphide of carbon was between 0° and 3°. The flame of a gas-lamp burning close to the apparatus was blue slightly tinged with violet, and spectrum analysis of this flame showed a persistent weak sodium line masking any other spectrum.

I only succeeded in realising these conditions by the care I took in dusting both rooms, and everything in them, two days previously, in having the floors carefully washed as well as the stairs, and in abstaining from working in the laboratory. When I did not take these precautions I always saw bright points in the flame.

Five drops of a 10 per cent solution of nitrate of silver caused a slight precipitate in 10 c.c. of filtered water. One drop of a saturated solution of chloride of barium, added to 15 c.c. of filtered water, gave no precipitate; but the mixture, when evaporated down to about half a c.c., became perceptibly clouded.

One hundred c.c. of filtered water left, on evaporation, a rich yellow stain weighing 0·000065 grm. The stain turned black when heated; the residue was dissolved by two drops of water, and the solution when put into the flame coloured it yellow, intensely but temporarily. Spectrum analysis showed the sodium line and a very faint calcium spectrum.

The inner filter, through which the water passed, when dried, was the same colour as paper exposed to the atmospheric dust of the laboratory. Under the microscope I saw a number of black and sparkling grey specks, as well as filaments. After burning the carbon made by carbonising the inner filter in a closed vessel, there remained a brown ash weighing 0·000105 grm. During combustion, the part of the flame affected was coloured deep yellow. The ash, when moistened with chloride of ammonium and put into the flame, showed sodium and calcium spectra, but not a trace of a potassium spectrum. The residue, when treated thrice with fluoride of ammonium to eliminate the silica, and put into the flame, still showed the sodium line without the potassium line. Lastly, the brown marks left on the fine platinum wire loop, when treated with pure sulphuric acid and put once more into the outer envelope of the flame, showed the sodium line still, with a very faint calcium spectrum, but no trace of the potassium line.

2nd. *Air from the street*, running east and west, entering by an opening on the south, by way of the roof and loft:—

The air brought into the laboratory by the draught of four ventilating shafts with which it was furnished, coloured a Bunsen flame distinctly violet; on spectrum analysis, a faint but decidedly yellow sodium line was seen, without a trace of the calcium spectrum; outside, the air temperature was 27·3°; in the glass case it was 23·8°, and dew-point was 17·7°; there were collected 135 grms. of filtered water, neutral to litmus-paper.

Five drops of a 10 per cent solution of nitrate of silver made a sensible precipitate in 10 c.c. of filtered water.

Twenty c.c. of filtered water were evaporated down to about half a c.c. This liquid was sensibly clouded by adding one drop of a saturated solution of chloride of barium.

One hundred c.c. of filtered water, when evaporated to dryness, left a sparkling brown stain, weighing 0·000057 grm. This residue blackened when heated; when dissolved in two drops of water, and put into a flame, the solution coloured it yellow. Spectrum analysis showed the sodium line, as well as a faint calcium spectrum.

The inner filter, through which the water passed, when dried, was the same colour as paper exposed to the dust of the laboratory; under the microscope it showed sparkling and transparent black and grey specks, stains just like clay, moistened and dried, as well as organic filaments, some long, others short.

After burning the carbon made by carbonising the filter in a closed vessel, there remained a brown siliceous ash, weighing 0·000147 grm. During combustion, spectrum analysis showed a strong sodium line. This ash, when moistened with chloride of ammonium, coloured the flame intense yellow, showed a sodium spectrum and a faint calcium spectrum all the time, but no traces of a potassium spectrum.

Having eliminated the free and combined silicic acid by means of fluoride of ammonium, then treating the residue with sulphuric acid, I detected in the product faint indications of the presence of sodium, calcium, aluminium, and iron; but I utterly failed to find any trace of potassium.

If we admit that the methods I adopted for ascertaining the nature and amount of sodium and calcium compounds in the air give correct results, we must conclude from them that air, when deprived by rain of the dust it had in suspension, and kept saturated or nearly so by rain, does not contain in from 10 to 15 cubic metres an amount of soluble sodium compounds capable of being weighed in a balance weighing to *three thousandths of a m.grm.* There is sodium in it nevertheless, although spectrum analysis of a Bunsen flame burning in it does not show the sodium line.

In this manner the presence of sodium is accounted for in hygroscopic bodies, other than sodium compounds, exposed to the air and sheltered from dust particles; for they—by liquefying it by absorption of, and depositing it by condensation of, the water in the air—persistently give indications of the presence of the metal sodium. Such are undoubtedly the chlorides of calcium and lithium, as I show in chapters devoted to the chemical and spectroscopic studies of these bodies. Neither outside nor inside air, *when still*, contains a measurable amount of soluble sodium compounds in from 10 to 15 cubic metres, although they give the sodic characteristics to flames. The quantity of insoluble sodium and calcium mineral matters in this amount of air varies from *six to fifteen hundredths of a m.grm.*

I have noted the presence of potassium amongst the mineral matters in free air in certain districts.

In spite of all efforts I cannot detect a trace of either soluble or insoluble potassium compounds in *the air of the higher part of Brussels.*

Rain Water.—I thought it useful to check my researches in air by making a comparative examination of the water condensed from saturated air, and rain water collected *when there was no wind.* I worked with rain which fell by day as well as by night, in order to better understand the part played by chimneys in contaminating the air.

The rain water was collected in the middle of the garden, 1 metre above the ground, after the air had been washed by several days' drizzle. Under these conditions it seemed that the rain water ought only to contain traces of the mineral matters in the clouds supplying the rain, to which would be added the compounds emanating from chimneys.

To collect the rain water, I put on a board, 1 metre above the lawn, five Bayeux porcelain dishes, 40 c.m. diameter. In addition I arranged, at a side of the yard leading to the garden, a cloth to shelter the spectroscope, Bunsen lamps, and everything I wanted to filter and evaporate the collected rain water. *All experiments on rain water were conducted in the open air, which was saturated with moisture but not misty.* As it was collected the water was poured into a covered platinum vessel, and filtered after weighing. I used for this purpose double filter-papers, which were first treated with dilute and pure nitric and hydrofluoric acids, and finally with water. The double filter-papers were arranged in a platinum funnel passing through a hole in a sheet of polished glass on a platinum retort, in which was collected the weighed and filtered water.

To ascertain the nature and quantity of matters either dissolved or left in the filter, I did as I have described above with water condensed from the vapour in the air.

Whilst I was collecting the rain water I worked the condensing apparatus outside the window on the second floor and sheltered from the rain, so as to be able to compare both results.

Rain Water fallen during the Day.—Wind, none; temperature of the air, 8·13°; rain water collected between 8 a.m. and 3 p.m., 153 grms.

All day long the Bunsen lamp burnt in the yard, *under the canvas*, which was quite soaked with the rain, without showing a trace of the sodium line on spectrum analysis. It was the same outside the second floor window under cover, where the apparatus for condensing the atmospheric moisture was working. Dew-point was 7·90°. The water collected weighed 138 grms.

The filtered rain water was colourless, and *neutral* to litmus-paper. When sprayed into a Bunsen flame, burnin the court under the wet canvas, by means of a metallic injector with steam from pure water, it turned the flame distinctly *yellow.* Spectrum analysis of the yellow flame showed the sodium line, hitherto invisible in the flame burning in air, or in the flame with *pure* water coming from the spray, which had been purified from sodium dust.

Five drops of a 10 per cent solution of nitrate of silver made a very decided precipitate in 20 c.c. of filtered *rain water.* Five drops of a 10 per cent solution of nitrate of silver made a very slight cloudiness in 20 c.c. of filtered *water of condensation.* One drop of a saturated solution of chloride of barium gave no precipitate in 10 c.c. of filtered rain water. After evaporating 20 c.c. of rain water down to about half a c.c., the residue was very slightly clouded by one drop of a saturated solution of chloride of barium; whereas after evaporating 18 c.c. of *water of condensation* down to about half a c.c., the residue was not affected in the slightest degree by one drop of a saturated solution of chloride of barium.

Filtered rain water, when being evaporated on a bath, emitted a smell of fog similar to that noticed after rain. One hundred c.c. of this water, when evaporated down to about 1 c.c., yielded a cloudy brownish yellow liquid. This liquid, when evaporated to dryness on the bath, left a brown hygroscopic residue weighing 0·000191 grm., whilst 100 c.c. of *water of condensation* left a brown stain weighing only 0·000027 grm. The residue left, after evaporating the rain water to dryness, turned very black, and emitted a smell like coal-tar, when raised to a dull red heat in a closed vessel. This residue, when dissolved by a few drops of water and put into a Bunsen flame, coloured it yellow, and showed on spectrum analysis a brilliant but temporary sodium spectrum, as well as a weak and incomplete calcium spectrum, *but no trace of the potassium line.*

The filter through which the rain water had passed, when dried, showed a dark grey tint all over its surface, a vast number of black specks, and also filaments. When carbonised in a closed vessel, and then burnt, it left a reddish brown siliceous ash, weighing 0·000225 grm. per 100 c.c. of filtered water.

During combustion I saw the sodium line, but no trace of a calcium or potassium spectrum. When moistened with chloride of ammonium, the ash showed an ill-defined sodium and a very weak calcium spectrum. After eliminating the free and combined silicic acid by means of fluoride of ammonium, and then treating it with sulphuric acid, I still saw a sodium and a very weak calcium spectrum, but no potassium line.

The inner filter, through which the *water of condensation* from atmospheric vapour had passed, when dried, carbonised, and burnt, left 0·000042 grm. of brown siliceous ash, containing sodium and slight traces of calcium; but I could not detect the presence of potassium in it by spectrum analysis.

Rain Water fallen during the Night.—There had been a fine rain all night, but no wind. The results of the experiments were of the same nature as those above. For instance, it was necessary to concentrate the filtered water to $\frac{1}{100}$th of its volume in order to detect, with nitrate of silver, the presence of chlorine, and to $\frac{1}{50}$th of its volume to prove the presence of sulphuric acid by means of chloride of barium.

The residue, after evaporating 100 c.c. of filtered water, was brown and weighed 0·000115 grm., and consisted chiefly of tarry matters, with traces of volatile compounds of sodium and calcium, but not of potassium.

The filter through which the nocturnal rainfall had passed was considerably less stained than that used to filter rain fallen during the day, and the weight of the brown ash left on burning it was only 0·000098 grm. per 100 c.c. of filtered water,—that is to say, less than half the weight of the ash of the filter through which an equal volume of rain water collected by day had passed, which was 0·000225 grm.

This last fact tends to show that, *when there is no wind*, the chimneys contribute largely to the contamination of the air by the mineral matters which are found in it near crowded neighbourhoods, and that the remainder may perhaps be attributed to rain clouds. But before coming to a general conclusion these experiments ought to be tried a great number of times, and this can hardly be done excepting in a building fitted up for meteorological research.

I ascertained, besides, by many trials, that the rain entrapped the soluble and insoluble matters suspended in the air so thoroughly, that, after very heavy rain, *the last showers* gave water so free from chlorides and sulphates that I had to evaporate it down to $\frac{1}{200}$th of its original volume before I could detect chlorine and sulphuric acid in it by nitrate of silver and chloride of barium. During the summer of 1881 I not only found that chlorine and sulphuric acid were not present in the rain which fell at the end of a very heavy storm, but after the rain ceased I found the outer air left for several hours during the day in such a state of purity that it was absolutely impossible to detect a trace of the sodium line in the spectrum of a Bunsen flame burning in it.

With very rare exceptions coal and coke are used in Brussels as fuel; I attribute to this the absence of potassium, for it has been detected in the atmospheric dust of other districts.

I think it is scarcely necessary to mention that the results given above are only applicable to the atmospheric conditions existing at the time of my experiments. In truth, long experience has taught me the great variation in the nature of atmospheric dust, according to the prevailing winds. I cannot say that I have on a single occasion found the air of the higher part of the town the same twice running as regards dust. The air appears most free from mineral dust after a fine rain without wind, and whilst it continues raining. In this case the suspended dust particles are always blackened by coal-smoke.

I have ascertained beyond a doubt, by observations extending over more than a third of a century, that the dust brought by the air, with or without rain, shows a density of colour, always varying according to the direction of the wind which brings it.

The air which passes over the town from the north or north-west, towards the south or south-west before reaching the street in which I live, always brings with it a fine siliceous dust more deeply blackened by coal-smoke than that entrapped by the fine rain which falls when there is no wind. The air brought by a south or south-east wind, with or without rain, brings a greasy, more or less yellow, dust.

Lastly, the air brought by an east wind, with or without rain, brings a grey dust, with a sandy, clayey character.

According as buildings are raised in my neighbourhood, which was originally quite open, on the east, south, or south-west, so have the physical properties of dust deposits remarkably changed, without, however, attaining each other's specific characteristics.

The facts I have mentioned here ought to be met with in all districts. Whenever accurate observations are made everywhere, no doubt we shall find that they are due to the dust of the air as well as to the water which flows along the ground, abstracting from it the soluble bodies it contains, no matter what may be the nature or origin of these bodies.

The nature of the dust particles ought to have some connection with the composition of the soil swept by the wind, and the smoke poured into the air by factories and chimneys.

(To be continued).

King's College.—Free Lecture.—On Monday next, the 9th inst., a Free Lecture will be given to the Public, in the Theatre of the College, by Prof. Thomson, F.C.S., &c., on "Movements of Gases and Liquids" (Experimentally Treated), commencing at 8 p.m.

On the Neutral Crystalline Calcium Chromite.—E. Dufau.—At a sufficiently high temperature chromium sesquioxide combines directly with lime, forming a chromite of the formula Cr_2O_3CaO. It is crystalline and stable at the highest temperatures. Its specific gravity is 4·8 at 18°, and it resists the action of the most powerful acids.—*Comptes Rendus*, cxxi., No. 20.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 266).

125. "*Normal Hexane from Light Petroleum* (*Petroleum Ether*)." By G. L. THOMAS, B.Sc., and SYDNEY YOUNG, D.Sc., F.R.S.

Having devised an improved form of dephlegmator (CHEMICAL NEWS, lxxi., 177) we determined to attempt the separation of a pure paraffin from "petroleum ether" in the same way that ethyl acetate was separated from a mixture of methyl, ethyl, and propyl acetates (*Phil. Mag.*, 1894, 8).

Each fraction was weighed, and its temperature range noted and corrected for the thermometric error and for the difference between the barometric reading and 760 m.m. The ratio of the weight of any fraction (Δw) to its temperature range (Δt) gives, as a rule, a measure of the purity of the liquid, though in the early fractionations of a complex mixture this csnnot be relied on.

Thus, in the 4th fractionation the fraction coming over between 65·0° and 66·0° had the highest value of $\Delta w/\Delta t$, whereas in the 16th fractionation the corresponding fraction (65·0° to 66·85°) had the lowest value. At an early stage of the work it appeared, therefore, as though a single substance boiling at about 65° or 66° was being separated from liquids boiling at much higher and lower temperatures (above 90° and below 40°); but the later fractionations showed that instead of a single substance boiling at about 65° or 66°, there were really two liquids —one boiling at 69°, and the other at about 61° (normal and iso-hexane).

As the number of fractions was very large, it was decided after the 16th fractionation to proceed only with the separation of normal hexane, and after 31 preliminary fractionations it was considered that the separation had proceeded far enough for the final series of fractionations to be undertaken, as in the case of ethyl acetate (*loc. cit.*). The hexane obtained by the final fractionation of the fractions boiling at and above 69·05°, when distilled from phosphorus pentoxide, boiled at 69·1°, or only 0·1° higher than the hexane prepared from propyl-iodide, but its sp. gr. at 0° (0·68478) was 1·15 per cent higher. The hexane was then treated with a mixture of concentrated sulphuric and nitric acids, when considerable heat was evolved, and the acid became yellow, and was found to contain some *m*-dinitrobenzene in solution. The impurity present was therefore benzene or possibly hexanaphthene, or both.

The remaining high-boiling fractions were treated with the mixed acids and were refractionated; the low-boiling fractions also were treated in the same manner before their final fractionation, and in every case it was found that *m*-dinitrobenzene was formed.

By further long-continued treatment of the two specimens of hexane with the mixed acids and subsequent distillation, a quantity was finally obtained boiling at 69·05° and with the sp. gr. 0·67813 at 0°, or only 0·17 per cent higher than that of pure hexane.

The vapour pressures and specific volumes—as liquid and as saturated vapour—were determined at a few temperatures, and the critical temperature and pressure were also observed; the results differed but slightly from those obtained with the hexane from propyl iodide. The critical constants of both specimens are given below:—

	Critical temperature.	Critical pressure.
Hexane from petroleum ether ..	235·15	22560
Hexane from propyl iodide.. ..	234·8	22510

The hexane was evidently very nearly pure, but the separation of this paraffin from petroleum ether is only possible by long-continued fractional distillation with an efficient dephlegmator, and by removal of benzene or hexanaphthene with nitric and sulphuric acids.

126. "*The Vapour Pressures, Specific Volumes, and Critical Constants of Normal Hexane.*" By G. L. THOMAS, B.Sc., and SYDNEY YOUNG, D.Sc., F.R.S.

The normal hexane employed was obtained from Kahlbaum, and prepared by the action of sodium on propyl iodide. It was purified by treatment with concentrated nitric and sulphuric acids and subsequent fractional distillation.

The boiling-point at 760 m.m. is 69·0°, and the sp. gr. at 0° is 0·67696. The critical constants are—

Critical temperature	234·8°
Critical pressure	22510 m.m.
Critical volume of a grm...	4·268 c.c.

The vapour pressures and the volumes of a grm.—as liquid and as saturated vapour—were determined, and a limited number of observations of pressure and volume of unsaturated vapour were made at a series of temperatures with the object of finding whether the isochors showed any indication of curvature. As in the case of isopentane (in about the same volume region) the isochors were found to be very slightly curved, the values of dp/dt diminishing with rise of temperature. The deviations from constancy become smaller as the volume increases.

The absolute temperatures and molecular volumes of liquid and saturated vapour were read from the curves at a series of pressures "corresponding" to those given in previous papers, and the ratios of the absolute temperatures and of the volumes to the critical constants were calculated. These ratios agree with those of isopentane and benzene; normal hexane therefore belongs to Group I. in the classification of substances previously adopted (*Trans. Chem. Soc.*, lxiii., 1257; *Phil. Mag.*, 1894, 1), and the molecules of the liquid are probably simple like those of the gas.

The absolute temperature ratios at corresponding pressures are higher for hexane than for isopentane; in this respect the paraffins seem to resemble the esters (*Trans. Chem. Soc.*, lxiii., 1252), for which the ratios increase without exception with rise of molecular weight. In the case of the esters, the volume ratios appear to be independent of molecular weight, but—for isomeric compounds—to depend to some extent on the constitution. It seems probable that this may also be the case for the two paraffins studied, but an investigation of other paraffins will be necessary before these points can be decided.

The ratio of the actual to the theoretical density at the critical point is 3·83, the mean value for the other members of Group I., including carbon dioxide (Amagat) and isopentane, being 3·75.

127. "*Acidylthiocarbimides.*" By AUGUSTUS E. DIXON, M.D.

This paper gives an account of further experiments (see Dixon and Doran, *Trans. Chem. Soc.*, 1895, lxvii., 565) on the production of thiocarbimides containing acidic radicles. By heating the chloride of valerianic or of cinnamic acid with lead thiocyanate in presence of anhydrous benzene, valeryl or cinnamoyl thiocarbimide is formed, and passes into solution. Both these thiocarbimides have a slightly pungent odour, and attack the eyes, causing a flow of tears, the former being especially active. They are readily desulphurised by lead or silver salts, but decompose in presence of water, yielding thiocyanic acid, together with the acid characteristic of the thiocarbimide,—

$$\begin{aligned}&\mathrm{Ph{\cdot}CH{:}CH{\cdot}CO{\cdot}NCS + H_2O =}\\&\qquad\mathrm{= HSCN + PhCH{:}CH{\cdot}COOH.}\end{aligned}$$

By bringing the solutions into contact with ammonia, amines, or ethyl alcohol, the corresponding thioureas, thiocarbimides, or thiourethanes, respectively, are produced.

The following compounds are described :—

ab-*Valerylphenylthiocarbamide*, $BuCO\cdot NH\cdot CS\cdot NHPh$; sym. *valerylphenylurea*, $BuCO\cdot NH\cdot CO\cdot NHPh$; ab-*valerylorthotolylthiocarbamide*, $BuCO\cdot NH\cdot CS\cdot NH\text{-}o\text{-}To$; sym. *valerylorthotolylurea ;* ab-*valerylparatolylthiocarbamide*, $Bu\cdot CO\ NH\cdot CS\cdot NH\text{-}p\text{-}To$; *valeryl-α naphthylthiocarbamide*,$BuCO\cdot NH\cdot CS\cdot NH\cdot\alpha\text{-}Napt$; n-*valeryl-v-benzylphenylthiourea*, $PhCH_2\cdot N(Ph)\cdot C(SH{:}N\cdot COBu$; *valerylthiourea*, $CSN_2H_3\cdot COBu$; *valeryl - β - thiourethane*, $BuCO\cdot NH\cdot CS\cdot OC_2H_5$; ab - *cinnamoylphenylthiocarbamide*, $PhCH{:}CH\cdot CO\cdot NH\cdot CS\cdot NHPh$; ab-*cinnamoylorthotolylthiocarbamide*, $PhCH{:}CH\cdot CO\cdot NH\cdot CS\cdot NH\cdot o\text{-}To$; ab. *cinnamoylparatolylthiocarbamide*,—

$$PhCH{:}CH\cdot CO\cdot NH\cdot CS\cdot NH\text{-}p\text{-}To;$$

ab·*cinnamoylalphanaphthylthiocarbamide*,—

$$PhCH{:}CH\cdot CO\cdot NH\cdot CS\cdot NH\alpha Napt;$$

cinnamoylthiourea.—

$CSN_2H_3\cdot COCH{:}CHPh$; $PhCH{:}CH\cdot CO\cdot NH\ CS\cdot OC_2H_5$, *cinnamoyl·β-thiourethane*. All the thioureas above named, with the exception of the valeryl benzoylphenyl compound, are desulphurised by heating with alkaline lead tartrate.

It is proposed to extend these experiments with lead thiocyanate, in the hope of obtaining thiocarbamides derived from other acids than those only containing the group $CO\cdot Cl$; for example, picric, phenylsulphonic, and ethyl sulphuric acids.

128. "*Some Constituents of the Root of* '*Polygonum cuspidatum*.'" By A. G. Perkin.

Polygonum cuspidatum is a native of China and Japan, and flourishes in parts of India and Russia. The freshly gathered roots consist of a thick, succulent bark, of an orange-red colour, and a central woody portion of a light yellow tint.

The principal constituent of the root bark was found to be a glucoside, $C_{21}H_{20}O_{10}$, crystallising in lustrous yellow needles melting at 202—203°. On hydrolysis, this yielded 61·82 per cent of a product which was recognised as *emodin*, the reaction—

$$C_{21}H_{20}O_{10}+H_2O=C_{15}H_{10}O_5+C_6H_{12}O_6$$

requiring 62·5 per cent of emodin. This glucoside, for which the name *cuspidatin* is proposed, differs considerably in properties from frangulin, $C_{21}H_{20}O_9$, the glucoside of emodin which is contained in the bark of the *Rhamnus frangula*.

A second glucoside was also isolated, but in too small quantity for analysis. On hydrolysis it yielded a crystalline substance melting at 199°, which by treatment with sulphuric acid at 160° was converted into emodin. It was found to be identical with the emodin monomethyl ether previously isolated from the root bark of *Ventilago madraspatamæ* (*Trans. Chem. Soc.*, 1894, 923). The other substances found were a small amount of free emodin and a wax which crystallised in colourless leaflets melting at 134—135°. This latter was found to be identical with the wax $C_{18}H_{28}O$, present in the root bark of the *Morinda umbellata* (*Trans. Chem. Soc.*, 1894, 854).

An examination is being carried out of the constituents of the roots of the *Polygonum bistorta* and *Rumex nepalensis*, which are closely allied to this plant.

129. "*Note on the Action of Hydrofluoric Acid upon Crystallised Silicon*." By G. S. Newth.

It is generally stated that hydrofluoric acid is without action upon crystallised silicon; that while amorphous silicon is attacked by it, this acid is incapable of acting upon the crystallised element.

This statement, however, requires to be made with some reservation, for although it is doubtless true of the aqueous acid, and possibly of the liquid acid, it is not true of the gas.

If acid potassium fluoride be heated in a platinum retort, and the pure gaseous hydrofluoric acid so produced be allowed whilst hot to blow upon a little heap of crystallised silicon supported on a porcelain crucible lid, the silicon at once takes fire and burns brilliantly in the gas, forming silicon fluoride and hydrogen.

If the neck of the retort be more than an inch or two in length, it is necessary to heat it in order to keep the gas sufficiently hot, but if it be quite short, the temperature of the gas as it is disengaged from its compound is sufficiently high to enable it to attack the silicon.

The importance of this observation lies in the fact that the spontaneous ignition of crystallised silicon is generally regarded as in all cases a sufficient test for free fluorine; but it is evident that unless the temperature of the gas is below a certain point the combustion of silicon is not a safe criterion.

130. "*Note on the Periodides of Theobromine.*" By G. E. Shaw.

Apparently only one periodide of theobromine has been previously described, viz., that having the formula $C_7H_8N_4O_2\cdot HI\cdot I_3$, prepared by Jörgensen by exposing a solution of theobromine hydrochloride, mixed with potassium iodide, to the air. By varying the amounts of hydrochloric and hydriodic acids present, the author has obtained compounds having the formulæ—

$$(C_7H_8N_4O_2)_2HI\cdot HCl\cdot I_2 \text{ and } (C_7H_8N_4O_2)_3HI(HCl)_2I_3,$$

and by re-crystallisation of a mixture of the three from weak alcohol containing hydriodic acid and iodine, a substance of the composition $(C_7H_8N_4O_2HI)_2+H_2O$ was obtained.

A solution of theobromine in saturated hydriodic acid deposited on standing crystals having the composition $(C_7H_8N_4O_2HI)_2I_3$.

131. "*A Synthesis of Diphenyloxytriazoline.*" By George Young, Ph.D.

The reaction between benzaldehyd and phenylsemicarbazide described in a previous notice (*Proc. Chem. Soc.*, 1894, 95, 124), and represented by the equation $C_7H_9N_3O+C_7H_6O+O=C_{14}H_{11}N_3O+2H_2O$, is shown in the present paper to take place in the following two stages : — I. $C_7H_9N_3O + O = C_7H_7N_3O + H_2O$; II. $C_7H_7N_3O+C_7H_6O=C_{14}H_{11}N_3O+H_2O$. The intermediate product, $C_7H_7N_3O$, is phenylazocarbonamide, $C_6H_5N{:}N\cdot CO\cdot NH_2$. It is formed immediately by the action of ferric chloride in aqueous solution, or potassium permanganate in dilute sulphuric acid. It is also formed, but very slowly, by the action of moist air on phenylsemicarbazide. It forms red needle-shaped crystals, m. p. 114°. The second stage of the above reaction does not take place so easily when the intermediate product is isolated as when the benzaldehyd is added to the phenylsemicarbazide before oxidation. In the latter case, the whole reaction takes place in boiling alcohol; in the former, the azo-derivative and the benzaldehyd require to be heated in alcohol in a sealed tube at 120° C. The benzoyl-derivative,—

$$C_{14}H_{10}N_3O(C_7H_5O),$$

has been prepared, in addition to those previously mentioned, by the action of benzoyl chloride on diphenyloxytriazoline and its silver salt. It forms flat needles, m. p. 133·5°.

132. "*Note on Piperovatine.*" By Wyndham R. Dunstan, F.R.S., and Francis H. Carr.

The method previously used (*Trans.*, 1895) for extracting piperovatine from *Piper ovatum* being exceedingly tedious, the authors experimented with the view of finding a better method. The following process is a considerable improvement, and with its aid the active constituent can now be extracted and crystallised in the course of a few hours. The method consists in percolating with ether; the dark-coloured extract thus obtained is freed from ether and the adhering volatile oil, and then extracted with hot dilute alcohol (13 per cent); on cooling this extract, crystals separate, which may be re-crystallised from 40 per cent alcohol.

Further experiments have been made on the hydrolysis of piperovatine with the small remaining quantity of material. A small quantity was heated with water in a sealed tube to 160°, with the result that a volatile base, probably a pyridine derivative, a substance smelling like anisol and giving phenol, on treatment with sodium hydroxide, and also an acid were produced.

133. "*Dibenzaconine and Tetracetylaconine.*" By Wyndham R. Dunstan, F.R.S., and Francis H. Carr.

The authors having failed so far to produce aconitine by the acetylation of benzaconine have tried to form benzaconine by introducing a benzoyl group into aconine; this, however, has not yet been contrived, but new aconine derivatives have been obtained. When equimolecular proportions of aconine and benzoic anhydride are dissolved together in chloroform and allowed to stand at the ordinary temperature, reaction occurs with production of dibenzaconine.

Dibenzaconine, $C_{24}H_{37}(Bz)_2NO_{10}$, is unlike aconine in being insoluble in water and soluble in ether; it crystallises from ether in rosettes of needles, m. p. 265°. *Dibenzaconine hydrobromide* crystallises well from a mixture of alcohol and ether, m. p. 261°. *Dibenzaconine aurichloride* is precipitated by adding a solution of gold chloride to a solution of the hydrochloride of the base, and may be crystallised in yellow tables from a mixture of alcohol, ether, and petroleum, m. p. 212°. This salt contained 18 2 per cent of gold; calculated for $C_{24}H_{37}(Bz)_2NO_{10}HAuCl_4$, 18·71 per cent. Hydrolysis of the base furnished 33·3 per cent of benzoic acid; the calculated quantity for $C_{24}H_{37}(Bz)_2NO_{10}$ is 34·4 per cent.

By the action of a large excess of benzoic anhydride, a crystalline base, m. p. 190°, soluble in ether and insoluble in water, is formed, which has not been further examined. Benzoyl chloride dissolved in chloroform does not react with aconine even when heated with the base.

Tetracetyl-aconine is formed when a solution of aconine hydrochloride and acetyl chloride in chloroform is allowed to stand for thirty-six hours at the ordinary temperature. It is insoluble in water, but readily soluble in ether and in alcohol, from either of which solvents it crystallises in small prisms, m. p. 196°.

On hydrolysis, aconine and 35·2 per cent of acetic acid are formed, the formula $C_{24}H_{35}(Ac)_4NO_{10}$ demands 35·8 per cent of acetic acid.

134. "*Molecular Volume Change during the Formation of Dilute Solutions in Organic Liquids.*" By A. Wentworth Jones, M.A.

The author has determined the volume changes during the formation of several solutions in benzene and carbon disulphide, and calculated the molecular volume change as $v \times m \times W/V \times M \times w = x$.

Where v = observed volume change,
V = volume of solution,
m = molecular weight of substance,
w = weight of substance taken,
W = ,, solvent ,,
M = molecular weight of solvent,
and x = ,, expansion or contraction.

The values for molecular weights of several "non-associating" liquids are very different, and sometimes change their sign, and if the phenomena of these solutions in organic liquids are comparable with those of aqueous solutions of organic compounds, it is impossible to admit that these volume changes are measurements of the attraction of substance for solvent and equal for molecular weights of different substances, as is stated by Traube (*Ber.*, 1895, xxviii., 410).

The author suggests that these volume changes occurring on solution are of the same nature as the smaller changes occurring when a moderately strong solution is diluted, and that both are analogous to the deviations from Boyle's law observed in the case of gases.

The following values have been obtained by the use of the specific gravity method:—

Carbon Disulphide Solutions at 15° C.

	Molecular expansion.
Methyl formate	0·0797
Ethyl acetate ..	0·0809
Ethyl acetoacetate	0·1072
Paraldehyd ..	0·0972
Nitrobenzene ..	0·0349
Benzaldehyd ..	0·0305
Aniline	0·0310
Benzene	0·0320
Ethyl iodide ..	−0·0632
Phosphorus trichloride . ..	−0·0913

A contraction occurs in the last two.

Benzene Solutions at 15° C.

	Molecular expansion.
Methyl formate	0·0156
Ethyl acetate ..	0·0076
Ethyl acetoacetate	0·0120
Paraldehyd ..	0·0141
Nitrobenzene ..	−0·0040
Benzaldehyd ..	−0·0042
Aniline	−0·0067
Carbon disulphide	0·0188
Piperidine ..	0·0020
Phosphorus trichloride . ..	0·0041

A contraction occurs in the 5th, 6th, and 7th cases.

NOTICES OF BOOKS.

Milk, its Nature and Composition: a Handbook on the Chemistry and Bacteriology of Milk, Butter, and Cheese. By C. M. Aikman, M.A., D.Sc. Crown 8vo. Pp. 180. London: A. and C. Black. 1895.

A treatise on milk, as a commercial article of food, without a notice of the bacteria which affect its preservation, modify its properties, and in some cases serve as a *materies morbi*, would in these days be rightly set aside as comparatively worthless. Dr. Aikman has therefore done well to devote a chapter to the bacteria of milk, and elsewhere to notice the presence and the influence of micro-organisms on butter and cheese.

We find here, in the first place, an account of the structure of the cow's udder and of the secretion of milk. Dr. Aikman refutes the old theory that milk is filtered blood. He points out the important chemical difference that sodium salts predominate in the blood, whilst potassium salts are more abundant in milk.

An important chapter is devoted to the percentage composition of milk. A table shows the variation in the composition of cows' milk, as determined by different authorities. The average of fat in the German samples is, according to Fleischman, 3·40; according to Kirchner, 3·4; whilst in American samples it is 4·00; and in English milks the average of 120,540 samples is, according to Vieth, 4·10.

Milk, the author rightly holds, should be defined under a Sale of Foods Act as the "*normal* secretion of the mammary glands of the cow, and that a person selling *abnormal* milk should be treated as a sophisticator."

The official standard in England is only 3 per cent, whilst in Massachusetts it is 3·70, in Vermont 3·25, and in Philadelphia 3·50.

The three largest mineral constituents found in milk are potash, lime, and phosphoric acid, each forming from 20 to 26 per cent of the total ash.

The fat in the milk of different herds of cows varies no little. In the milk of short-horns it is 3·73, in Jerseys 5·02, in Guernseys 4·90, and in Ayrshires 4·15. We have not been able to meet with an analysis of a trustworthy specimen of the milk of Lancashire long-horns, but we believe it is at least as rich in fat as that of the Ayrshires.

Dr. Aikman does not accept the view that the richness of a milk in fat is shown by the depth of the layer of cream. He rejects the belief that thunder turns milk sour.

On the importance of cleanliness in every department of the milk trade the author insists most emphatically, showing how the hands of milkmen, the teats of cows, and the milk pails become rapidly contaminated.

The importance of milk as a vehicle of various diseases is carefully shown. Tuberculosis, typhus, diphtheria, and cholera are thus conveyed. According to Hart, of fifty epidemics of typhus investigated in England, twenty-eight were traced to infected milk.

We cannot prolong our survey of this valuable work, but we can conscientiously recommend it to all persons connected with the milk industries.

The Handling of Dangerous Goods: a Handbook for the Use of Government and Railway Officials, Carriers, Shipowners, Insurance Companies, Manufacturers and Users of such Goods, and others. By H. Joshua Phillips, F.I.C., F.C.S. Crown 8vo., pp. 362. London: Crosby Lockwood and Son. 1895.

The number of substances dangerous from one or other point of view which are met with in modern commerce is great. As a consequence, accidents to property and to human life are constantly occurring, due sometimes to the ignorance or the recklessness of manufacturers and merchants, and perhaps more frequently to the negligence of their servants. Hence Mr. Phillips has done well in presenting the public with the work before us. He is already favourably known to many of our readers by his works on "Engineering Chemistry" and on "Fuels, their Analysis and Valuation," and in his former capacity as consulting chemist to the Great Western and Great Eastern Railways he has enjoyed special opportunities of studying the classes of goods here under consideration.

The first part of the book treats successively of combustible acids, alkalies, salts, and gases, of coal-tar and its products, of petroleum and its products, of fixed oils and fats, of volatile oils and of various highly inflammable liquids, of inflammable solids, of substances liable to spontaneous combustion, and of explosives. These chapters are exceedingly well written, and, if duly studied and acted upon by the interests concerned, will be productive of much good. Some substances, however, are mentioned which are of little importance, such as vasolene. As for roasted and ground coffee, their importation and carriage by railway, if it ever occurs, is an evil; and as for date-stones and olive-kernels, they should never be allowed to be landed. The author does not mention ground dye-woods, the storage of which is often dangerous. Worst of all substances liable to spontaneous combustion are weighted or loaded silks, of which Insurance Companies should beware. The methods laid down for ascertaining the safety of explosives are those in practical use.

The Explosives Act of 1875 is here given at some length, together with the comments of Sir F. Abel. In some cases the penalties enacted for the offences against the provisions of the Act are unreasonably low.

The second part of the work narrates a series of accidents which are well named "instructive," and which may serve as a salutary lesson to persons who have to handle dangerous goods. It appears, from the Bombay calamity of 1891, that blasting gelatin is—especially in hot climates—liable to spontaneous decomposition. The dynamite catastrophe of Santander (1893) seems to show that the possible gains derived from high explosives are not enough to compensate for their evil results.

The number of accidents from mineral oil lamps is alarming, and it is especially to be regretted that such lamps while burning are frequently thrown at each other by persons quarrelling.

The intentional outrages effected in many cases by "Atlas powder A" exhibit a black record. Here, also, the perpetrators when detected too often escape with inadequate punishment.

The third part of the work gives the special railway classification, mode of packing, &c., for the conveyance of explosives by goods trains. Some of these classifications are open to objections.

An Appendix, containing a variety of useful tables, concludes the work.

The "Handling of Dangerous Goods" merits a wide circulation, and an intelligent, appreciative study.

Laboratory Manual of Inorganic Preparations. By H. T. Vulté and George M. S. Neustadt. New York: 1895. Pp. ii., 180, iii. 12 mo., Ill.

The authors of this useful handbook observe that the study of organic chemistry is usually conducted on a more logical plan than that of inorganic, synthetic work preceding analytical, and researches, and they propose that this work should be placed in the hands of students before they begin the study of analytical chemistry. It shows "how compounds, often very complex in character, rare in occurrence or expensive in preparation, may be produced from simple substances, or from those which are comparatively plenty and cheap, and how the bye-products may be saved." The substances to which the attention of the student is directed embrace water (ammonium-free), ethyl-alcohol, oxygen, hydrogen, nitrogen, chlorine, hydrochloric acid, nitric acid, nitrous oxide, and after several other mineral acids and oxides, compounds of calcium, lead, bismuth, of the alkalies, &c., as well as hydroxylamine, hydrazine, chydrazaïne, and carbonoxysulphide.

The instructions for preparing all these substances are clearly worded; perhaps the quantities taken are unnecessarily large in some cases, but this is a minor fault. References to original papers are often introduced, and equations expressing reactions are generally given when advisable.

In certain instances it is difficult to understand the reasons for selecting a given substance for study; but this remark would apply to any work of similar character, unless the reviewer happened to be the author as well.

The authors generally place the chemical formula of the substance under discussion at the head of each section, but not uniformly; they have taken pains to inform the student that hydrochloric acid has the formula HCl, but they neglect to inform him as to the composition of hydrazine, and of platinoso-chlorides, bodies presumably less known.

The work has an index, but lacks a table of contents.

The first-named of the authors has had experience in teaching large classes in the School of Mines, Columbia College, and undoubtedly knows the needs of students beginning the study of chemistry.

The handbook can be cordially recommended.—H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 20, November 11, 1895.

On Tempering Extra-Hard Steels.—F. Osmond.—If we take an ingot of steel carburetted by cementation in which the proportion of carbon varies in a continuous manner from end to end (say from 1·70 to 0·35 per cent), submit it to very energetic tempering, and then try with a sewing needle to scratch a polished surface, we find, as might be expected, that the needle scratches the softest parts up to about 0·70 per cent; the mark is then interrupted, but, contrary to all received ideas, it re-appears when the proportion of carbon exceeds 1·30 per cent. On examining this scratch in the most highly carburetted parts with the microscope it is found to be not continuous, but presents frequent interruptions. The region in question is therefore not homogeneous, and contains at least two constituents which we may call A and B. A, which is not scratched by the needle, scratches glass and orthose; B is scratched by apatite and perhaps by fluorspar. A has a slight greyish tint, whilst B is of a silvery whiteness.

On Nickel and Cobalt Silicides.—M. Vigouroux.—M. Moissan has recently made known the action of silicon upon iron, chromium, and silver. The author now describes nickel and cobalt silicides obtained in a similar manner. These silicides have a distinctly metallic aspect and a steel-grey colour perfectly crystalline. Nickel silicide has a specific gravity of 7·2 at 17°; cobalt silicide is 7·1 at the same temperature. They are more easily fusible than silicon or than the pure metals, but they resist the highest temperatures without decomposition. Fluorine attacks them with incandescence at the ordinary temperature. In dry chlorine they burn with incandescence at a red heat. The composition of the nickel compound is $SiNi_2$, and that of the cobalt silicide is analogous.

On the Alcoholates.—H. Lescœur.—The author describes the compounds $C_2H_5NaO,2C_2H_6O$, $C_2H_5N_2O$, $NaHO,C_2H_6O$, and $NaHO,3C_2H_6O$.

Properties of the Emulsine of Mushrooms.—Em. Bourquelot and H. Hèrissey.—One and the same emulsine appears to exist in the mushrooms, but we have as yet no evidence that it differs from the emulsine of almonds.

Constancy of the Congelation-point of some Liquids of the Organism.—J. Winter.—As regards milk the constancy of its congelation-point seems to me to afford a simple and certain check on its state of purity. This study reveals to us a novel and unknown function of the blood-globules or of the fibrine.

Fermentations induced by Friedland's Pneumo-Bacillus. — L. Grimbert. — The author's pneumobacillus differs from that of Frankland by its property of attacking glycerin and dulcite, by the nature of its fermentation-products, and by the energy of its action.

Direct Fixation of certain Metallic Oxides by Vegetable Fibres.—A. Bonnet.—The author finds that the copper, zinc, cobalt, and iron (ferric) hydroxides may be directly fixed upon vegetable fibres in conditions similar to those observed with the lead oxides.

Zeitschrift für Anorganische Chemie,
Vol. viii., Part 6.

Occlusion of Barium Chloride by Barium Sulphate.—T. W. Richards and H. G. Parker.—The occlusion af barium chloride by barium sulphate occasions considerable errors. The occlusion is greater in concentrated than in dilute solutions, greater in presence than in the absence of hydrochloric acid, and greater if the sulphate is added to the barium than in the inverse case. In the ordinary conditions of careful precipitation in presence of a slight quantity of free acid, the error occasioned by occlusion is nearly compensated by the solubility of barium sulphate in water or acids; this solubility must be taken into account in careful determinations. The error occasioned by occlusion can be corrected with great accuracy if the chlorine retained by the precipitate is determined and the corresponding weight of barium chloride is deducted from the total weight of the precipitate.

Colour, Specific Gravity, and Surface Tension of Hydrogen Peroxide.—W. Spring.—Hydrogen peroxide is a liquid of the same colour as water, though of a darker shade. Its specific gravity is 1·4996 and its surface tension smaller than that of water by more than one-half—3·582 as against 7·750. The colour which is shown by oxygen, in a higher degree by ozone, reappears in water and in hydrogen peroxide. All the facts seem to show that in H_2O_2 the oxygen has lost its characteristic attributes to a less extent than in H_2O. In a word, hydrogen peroxide seems in a chemical point of view to be rather a non-saturated compound between O_2 and H_2 than a true atomic compound. Hydrogen peroxide in a pure dry state decomposes no less violently than nitrogen chloride or nitro-glycerin.

Atomic Weight of Molybdenum.—Karl Seubert and William Pollard.—The authors find from molybdenum trioxide by the acidimetric process $Mo=95·729$, and by the reduction of the trioxide to metal $Mo=95·735$. The results of Dumas, Debray, Liechti and Kempe, Smith and Maas, and Seubert and Pollard yield a mean of 95·77, or if he bear in mind the uncertainty of the second decimal, $Mo=95·8$.

Heavy Metallic Salts of Bichromic Acid.—Gerhard Krüss and Oskar Unger.—The authors did not succeed in obtaining bichromates of the heavy metals in a definite form, but were merely able to produce crystalline double salts of metallic and alkali bichromates. The bichromates of the heavy metals are in general not capable of crystallisation.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 118.

The Smokeless Pyro-collodion Powder of Prof. Mendeleeff.—This lengthy paper does not admit of abstraction. It concludes with the well-known dictum: Si vis pacem para bellum.

Industrial Preparation of Liquid Air and Oxygen by means of the Linde Process.—This memoir requires the accompanying figures and the table of curves.

Tar of Naphtha.—This paper does not admit of useful abridgment.

MISCELLANEOUS.

Royal Society.—The following President, Officers, and Council were elected on November 30th last:—

President—Sir Joseph Lister, Bart., F.R.C.S., D.C.L.

Treasurer—Sir John Evans, K.C.B., D.C.L., LL.D.

Secretaries—Prof. Michael Foster, M.A., M.D.; The Lord Rayleigh, M.A., D.C.L.

Foreign Secretary—Edward Frankland, D.C.L., LL.D.

Other Members of the Council—William Crookes, F.C.S.; Sir Joseph Fayrer, K.C.S.I.; Lazarus Fletcher, M.A.; Walter Holbrook Gaskell, M.D.; William Huggins, D.C.L.; The Lord Kelvin, D.C.L.; Prof. Alexander B. W. Kennedy, LL.D.; Prof. Horace Lamb, M.A.; Prof. Edwin Ray Lankester, M.A.; Prof. Charles Lapworth, LL.D.; Major Percy Alexander MacMahon, R.A.; Prof. Jonn Henry Poynting, D.Sc.; Prof. Arthur William Rücker, M.A.; Osbert Salvin, M A.; Prof. Harry Marshall Ward, D.Sc.; Admiral William James Lloyd Wharton, C.B.

Royal Institution. — The following are the Lecture Arrangements before Easter: — Professor John Gray McKendrick, Professor of Physiology in the University of Glasgow, Six Lectures (adapted to a juvenile auditory) "On Sound, Hearing, and Speech" (experimentally illustrated); Professor Charles Stewart, Fullerian Professor of Physiology, R.I., Eleven Lectures on "The External Covering of Plants and Animals: its Structure and Functions"; The Rev. Philip H. Wicksteed, Four Lectures on "Dante"; Professor H. Marshall Ward, Professor of Botany in the University of Cambridge, Three Lectures on "Some Aspects of Modern Botany"; The Rev. William Barry, D.D., Four Lectures, "Masters of Modern Thought"—Voltaire, Rousseau, Goethe, and Spinoza; Professor C. Hubert H. Parry, Professor of Musical History and Composition at the Royal College of Music, Three Lectures on "Realism and Idealism in Musical Art" (with musical illustrations); The Right Hon. Lord Rayleigh, Professor of Natural Philosophy, R.I., Six Lectures on "Light." The Friday Evening Meetings will begin on January 17th, when a Discourse will be given by the Right Hon. Lord Rayleigh, on "More about Argon." Succeeding Discourses will probably be given by Professor Burdon Sanderson, Mr. W. S. Lilly, Dr. John Murray, Mr. J. J. Armistead, Dr. Edward Frankland, Mr. A. R. Binnie, Mr. Sidney Lee, Professor T. R. Fraser, Professor Dewar, and other gentlemen.

MEETINGS FOR THE WEEK.

Monday, 9th.—Society of Arts, 8. "Mechanical Road Carriages," by H. Worby Beaumont, M. Inst.C.E. (Cantor Lectures).

Wednesday, 11th.—Society of Arts, 8. Adjourned Discussion on Mr. Cunynghame's Paper on "Locomotive Carriages for Common Roads."

Friday, 13th.—Physical, 5. "A Mechanical Device for Performing the Temperature Corrections of Barometers," by Dr. John Shield. "On the Existence of Earth-Air Electrical Currents," by Prof. A. W. Rücker, F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXII., No. 1881.

ON THE GASES OBTAINED FROM THE MINERAL ELIASITE.

By J. NORMAN LOCKYER, C.B., F.R.S.

Observations have been made of the gases obtained from the mineral eliasite heated *in vacuo*, in the manner which I have described in a former paper (*Roy. Soc. Proc.*, lviii., p. 68), and, in addition to lines of known gases, others have been noted, for which no origins can be traced, at the following wave-lengths :—

Angström.	Rowland.
6121·2	6122·4
6064·5	6065·7
5990·0	5991·6
5874·9	5875·9 (D_3)
5845·7	5846·8
5428·8	5429·9
5403·1	5404·1

The wave-lengths of these lines have been determined by means of a Steinheil spectroscope having four prisms, comparisons being made with adjacent metallic lines, and the positions interpolated by micrometric measurements; the accuracy may perhaps be taken to be within 0·1 tenth metres. Other lines have been noted, but they are not included in the list, for the reason that their wave-lengths have not yet been determined with the dispersion stated above.

Of the lines in the foregoing list, six are in all probability coincident with chromospheric lines, as shown in the following table, which also indicates the frequencies and brightnesses of the lines according to Young :—

Wave-length of Chromospheric Lines.

(Angström's scale).	(Rowland's scale).	Frequency.	Brightness.
6121·2	6122·4	5	3
6064·5	6065·7	5	2
5990·0	5991·6	10	4
5874·9 (D_3)	5875·9	100	90
5428·8	5429·9	8	3
5403·1	5404·1	5	3

It is important to point out that all these lines do not appear in the spectrum at the same time. For instance, in the first two specimens of the mineral no trace of D_3 was noted, but in the third portion examined, all coming from the same specimen, D_3 appeared as a pretty bright line. Again, as in the case of a previous operation on bröggerite (*Roy. Soc. Proc.* lviii., p. 194), in one experiment with eliasite the products of distillation, collected in four stages, gave different spectra.

These facts seem to indicate that the gas obtained from eliasite is either a compound or a mixture of gases, just as is that obtained from bröggerite according to former experiments.

It is also to be remarked that among the lines in the eliasite spectrum, those at 6122·4 and 6065·7 have been recorded in the gases obtained from clèveite, and 6122·4 has also been noted in the gas obtained from gummite.

It seems to me more than probable, therefore, that the lines observed in eliasite indicate a new gas, in some way associated with those given off by clèveite and bröggerite, and the fact that D_3 is not necessarily present in the spectrum furnishes an additional argument in favour of the view that the gas obtained from clèveite or bröggerite is complex.

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[*] A Paper read before the Royal Society, November 21, 1895.

THE HISTORY OF MOND'S NICKEL EXTRACTION PROCESS.[*]

By LUDWIG MOND.

In the present paper I give an account of the history of my process of extracting nickel from its ores, as an instance of an investigation undertaken in pursuit of pure science, which has led unexpectedly, in a few years, to an important industrial application. I have often been asked by scientific men how I came to discover nickel carbonyl, and can now explain. Soon after I had satisfied myself that the ammonia soda process was far cheaper than the Leblanc process for producing carbonate of soda, it became evident to me that a time would come when the Leblanc process would produce carbonate of soda, as a by-product of the bleaching powder manufacture, which it would have to dispose of at any price it would fetch. I therefore undertook a series of experiments, with the object of producing bleaching powder as a by-product of the ammonia soda process. You all know that the usual form of this process consists in treating a solution of common salt in which caustic ammonia has been dissolved by carbonic acid, with the result that bicarbonate of soda is precipitated, while a solution of ammonium chloride is formed. In the ordinary course of things this solution of chloride of ammonium is distilled with caustic lime, yielding gaseous ammonia, which returns to the process and a solution of calcium chloride. Other investigators had endeavoured to produce chlorine from the chloride of calcium obtained by evaporating these solutions; others have proposed to substitute magnesia for the lime in distilling the solution of ammonia chloride, and to produce chlorine or hydrochloric acid from the $MgCl_2$ obtained by evaporating its solution. I gave my attention to producing the chlorine direct from the ammonium chloride, separated from the solution in which it is originally obtained by refrigeration.

Ammonium chloride when vapourised is, as is well known, dissociated into ammonia and H_4Cl; thus, if the vapour of NH_4Cl is passed over a metallic oxide, this oxide is converted into a chloride and the ammonia passes on altogether with the steam formed by the reaction.

I found that nearly all metallic oxides, with the exception of the alkalies and alkaline earths, and that even a large number of metallic salts, were acted upon in this way by NH_4Cl vapour, and that a large number of the metallic chlorides so formed would give up their chlorine by re-converting them into oxides by submitting them to the action of the air at a suitable temperature. I found that, of all the substances investigated, oxide of nickel yielded the best results, and that the next best were obtained by magnesia mixed with a certain amount of chloride of potassium.

In developing this process I had to construct a plant for volatilising NH_4Cl, which I found an extremely difficult problem, as the vapour of this substance not only acts on oxides and salts, but also violently attacks the large majority of metals. I succeeded in lining iron vessels with glazed tiles in such a way that they would withstand this action, but I required valves for changing from the current of ammonium chloride vapour to hot air, and *vice versa*, which had to be very tight to prevent a large loss of ammonia. I found that nickel was one of the few substances suitable for the construction of these valves, and that it was not at all attacked by ammonium chloride vapour.

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[*] Abstract of Paper read before the New York section of the Socisty of Chemical Industry.

These worked perfectly on a laboratory scale, but when applied on a manufacturing scale they became leaky, and the faces became covered with a black crust, which on examination was found to contain carbon. The source of this carbon seemed mysterious; the only difference between the work on the small scale and that on the large was that on the small scale we swept the ammonia out of the apparatus before admitting the hot air by means of pure CO_2, while on the large scale we used the gases from the lime-kiln containing a few per cent of CO. We found nickel to have the remarkable property of splitting off carbon from CO at a moderate heat, transforming it into CO_2.

In the course of the experiments finely divided nickel, formed by reducing nickel oxide at 400° C. by hydrogen, was treated with pure CO in a glass tube at varying temperatures for a number of days, and was then cooled down in a current of CO before it was removed from the tube. In order to keep the poisonous CO out of the atmosphere of the laboratory we simply lit the gas escaping from the apparatus. To our surprise we found that, while the apparatus was cooling down, the flame of the escaping gas became luminous, and increased in luminosity as the temperature got below 100° C. On a cold plate of porcelain put into this luminous flame, metallic spots were deposited, similar to the spots of arsenic obtained with the March apparatus, and on heating the tube through which the gas was escaping we obtained a metallic mirror while the luminosity disappeared. Upon examination of the mirrors we found them to consist of pure nickel. As it seemed improbable that so heavy a metal as nickel should form a readily volatile compound with CO we purified our CO as perfectly as possible, but still obtained the same results.

We now endeavoured to isolate this curious and interesting substance by preparing the nickel with great care at the lowest possible temperature, and treating it with CO at about 50° C., and thus we greatly increased the amount of the volatile nickel compound in the gases passing through the apparatus. We observed the excess of CO by cuprous chloride solution, and thus obtained a residue of several c.c. containing the volatile nickel compound mixed with a little nitrogen. By passing this gas through a heated tube we separated the nickel and obtained an increased flame of gas, and found in this a quantity of CO corresponding to about four equivalents for one equivalent of nickel. By further improving our method of preparing the finely divided nickel, and by passing the resulting gas through a refrigerator cooled by snow and salt, we at last succeeded in liquefying this compound, and were able to produce it with ease and facility in any quantity we desired.

This nickel carbonyl is a colourless liquid, boiling at 43° C., and which solidifies at −25° C., forming needle-shaped crystals. It is soluble in alcohol, petroleum, and chloroform; it is not acted upon by dilute acids or alkalis, and can be readily distilled without decomposition, But on heating the gas to 150° C., it is completely dissociated into its components, pure CO being obtained and the nickel being deposited in a dense metallic film upon the sides of the vessel in which it is heated.

After continued investigation I came to the conclusion that it ought to be possible to make use of the ease with which nickel is converted into a volatile gas by CO for separating nickel from cobalt and other metals on a manufacturing scale, and for obtaining it in a very pure state. We have now succeeded in producing nickel at the rate of 1½ tons per week, from the Canadian nickel matte imported into England. We erected a plant near Birmingham for this purpose. This matte, which contains about 40 per cent nickel and an equal quantity of copper, is carefully roasted, to drive out the sulphur as far as possible, and is then subjected to the action of hydrogenous gases, either water gas or producer gas rich in hydrogen, in an apparatus which is called the "reducer," the temperature of which is under perfect control, so that 400° C. is never exceeded. From this apparatus the substance which is now reduced to the metallic state is taken, through air-tight conveyors and elevators, into another apparatus called the "volatiliser," in which it is subjected, at a temperature not exceeding 80° C., to the action of CO gas. This apparatus consists of an iron cylinder divided into numerous compartments by shelves, and provided with a stirring device which moves the material from the top to the bottom, while the CO gas passes through in an opposite direction. The CO gas, which should be as rich as practicable, we prepared by passing pure CO_2 through incandescent coke; the pure CO_2 we make by passing the flue gas of a boiler or of a fire through a solution of carbonate of potash, and subsequently boiling the solution. The CO gas, charged with nickel carbonyl leaving the volatiliser, is passed through a series of tubes or chambers heated to about 180° C., in which the nickel is deposited in various forms, according to the speed of the gas current, the richness of the gas, and the existing temperature. The CO gas, thus almost completely free from the nickel, is taken back by means of a blower into the volatiliser, where it takes up a fresh quantity of nickel, and is constantly used over and over, so that the quantity consumed is limited to the very small amount of unavoidable loss through leakage of the plant.

The material under treatment is repeatedly dumped from the volatiliser to the reducer, and *vice versa*, by means of air-tight conveyors and elevators, until the amount of nickel volatilised begins to fall off. It is then roasted again, to remove the sulphur which it still contains, and is treated by sulphuric acid to dissolve part of the copper. The remaining mass, containing all the nickel, some copper, and the other impurities of the matte, is again subjected to the previous treatment until the nickel has been extracted as far as practicable, and the ultimate residue, still containing a few percentage of nickel, is melted up into matte again.

If the nickel is allowed to deposit slowly, at a carefully regulated temperature, it can easily be obtained from the gas as a coherent metallic flim, so that it is possible to coat any substance which can stand heating to 150° C. with a perfect covering of metallic nickel, and also to make articles of metallic nickel for direct use.

Hollow nickel goods can be made in this way, which at present either cannot be made at all or only by the use of very powerful hydraulic machinery, and this will give a great impetus to the manufacture of nickel utensils for domestic purposes, the use of which is so very desirable from a sanitary point of view. The cost of the process, if carried out on a sufficiently large scale, is inconsiderable.—*Engineering and Mining Journal.*

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 276).

Chapter III.

Chemical Researches on the Chloride, Chlorate, Perchlorate, and Chloroplatinate of Potassium.*

Introduction.

According to my experience up to the present, the molecular weight of chloride of potassium does not agree with Prout's hypothesis. Does this depend on the fact that the atomic weight of potassium is not a simple ratio of that of metallic silver which is used as the standard for comparison; or is it rather due to accidental impurities which might be in the chloride tested; or is it, lastly, that

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* This research was commenced in the month of December, 1878, and completed in 1882.

potassium is not an element? Such is the problem I endeavoured to solve by re-opening the study of chloride of potassium, which had already been the subject of lengthy investigations on my part.

In my *New researches on the laws of chemical proportions* I said "I must admit then that I could not prepare, by means of chlorate of potassium, a chloride which I could consider absolutely pure." In fact, after having successively eliminated the foreign matters contained in the purest chlorate of potassium, I detected, in the chloride made from it, the presence of silicon in the form of silica and alkaline silicates, and amongst them silicate of sodium in various quantities according to the conditions under which the chloride was produced. The total weight of silica and alkaline silicates was as much as 1-20,000th of the whole. When changing this chloride into chloroplatinate of potassium, I was able to decrease to one-half the weight of the residue left by volatilising chloride of potassium. As far as regards the silica and alkaline silicates, the minimum limit was then 1-40,000th of the whole. It was impossible for me to tell exactly the quantity of sodium existing in the chloride, or even the state in which the whole of this metal existed. I have always believed that the bulk was in the form of a silicate. Farther on I shall give the reason for this opinion. From my experience I can state that it is not always in the form of sodium chloride. In fact, by using a silver salt, it is possible, and even easy, to ascertain the presence of 1-10,000th part of chloride in a solution of chlorate or perchlorate of potassium in *pure* water. Now, a solution of these salts in absolutely pure water, which, on spectrum analysis, gives persistent and strong indications of the presence of sodium, remains absolutely clear, and, when exposed to light, *protected from atmospheric dust*, remains colourless, after having received a proper amount of nitrate or sulphate of silver,—a phenomenon which it is not possible to obtain with a solution of chlorate or perchlorate containing 1-10,000th of these salts. Bunsen, moreover, has shown that spectrum analysis discloses an amount of chloride of sodium 300,000 times less than that shown by using silver salts. The failure of chemists to procure, by crystallisation or otherwise, potassium salts which do not show the potassium line when volatilised in a colourless flame or in an electric spark, has led Mr. Lockyer to believe in the splitting up of potassium into sodium and another metal. I do not altogether agree with this hypothesis; the work I describe farther on is for the purpose of seeking what foundation it can have on fact, as much with regard to potassium as to other bodies, such as lithium, calcium, strontium, barium, thallium, silver, mercury, platinum, iridium, &c. Whilst admitting the possibility of procuring chloride of potassium absolutely free from sodium, silica, alkaline silicate, and all other known foreign bodies, what guarantee have we that the metal contained in it is truly an element?

When regarding it from the standpoint of experience actually acquired, there are as many reasons for considering the metallic base of this chloride to be an element as there are for considering the hydrogen in hydrochloric acid to be an undecomposable body. In short, the combinations and decompositions of the metal used in the reactions are always done in such a manner as to reproduce a body identical with itself, when submitted to chemical forces,—quite as powerful, in a different way, as physical forces,—exactly the same as hydrogen, no more, no less. The chloride from chlorate, and the chloride from chloroplatinate of potassium, though formed under very different conditions, are identical in all their properties. By my previous work I know that potassium, though it may form a chlorate, chloroplatinate, nitrate, or tartrate of potassium, is the same; it is represented by a *constant*. I think I am right in concluding, with most chemists, that potassium is as much an undecomposable body as hydrogen.

Wishing, however, to submit this conclusion to a new proof, I have had recourse to a second method of investigation. Before publishing, I beg to say that I had no confidence in the success of my undertaking. The search for knowledge and truth has throughout influenced my work.

If the metal contained in the chloride of potassium, formed by the dissociation of pure chlorate by the action of heat, be a simple undecomposable body, it seemed to me that, when submitting the chlorate to the action of heat, in such a manner as to reduce it partially into oxygen, chloride, and perchlorate of potassium, the proportion of chlorine to metal ought to be invariably the same in the chloride and in the perchlorate formed simultaneously with a similar chloride. The chloride which was made by the formation of perchlorate, and the chloride given off by the subsequent decomposition of this perchlorate, ought to be identical in every respect.

If, on the other hand, the metallic base of pure chlorate of potassium is a compound body, capable of being split up, the chloride and the perchlorate made by the dissociation of pure chlorate of potassium by the action of heat, ought to combine chlorine and the metal in different proportions, and the chloride made at the same time as the perchlorate ought to be different from the chloride made by the decomposition of this perchlorate.

As a matter of fact, chemical reactions do take place in this manner when we submit chlorate of potassium containing chlorate of sodium to the action of a suitable heat. When heating chlorate of potassium, mixed with 5 per cent of its weight of chlorate of sodium, in a platinum vessel, we find, after complete dissociation of the chlorates, nearly all the sodium in it in the form of chloride of sodium, in the resultant chloride of potassium. The platinum vessel is slightly attacked, forming a noticeable amount of chloroplatinate of sodium, as is always the case when one decomposes chlorate of sodium in platinum.

The perchlorate formed at the same time as the chlorides of potassium and sodium, contains only potassium. By a suitable treatment with alcohol, followed by successive crystallisations, repeated sufficiently often, in platinum vessels sheltered from atmospheric sodium, one can make the separation in such a manner as to obtain, on the one hand, chloride of potassium containing all the sodium, and, on the other, a perchlorate of potassium which behaves under spectrum analysis like all potassium perchlorate which has been long in contact with air, or rather in contact with a sodium compound more soluble than itself, and from which one has eliminated — by means of successive crystallisations and washings in alcohol—the sodium salt which was mixed with it.

Now if the metallic base of chlorate of potassium, in such a state of purity as I have been able to prepare it, is a compound body, one can reason by analogy that, by a properly regulated heat, the separation ought to take place in such a manner as to concentrate in the chloride or perchlorate, the whole—or at least a part—of one of the components of the metallic base of the chlorate.

The chemical *constant* of bodies being different, experience shows that the proportion of chlorine to metal in a chloride and a perchlorate ought consequently to be different, and to be between the limits of these constants. For the purpose of ascertaining what the real facts are, I started a long course of investigation.

I tried first whether it was possible to obtain chlorate of potassium which would not show the sodium line, and would be capable of being made to yield a chloride quite free from bodies, whether solid or volatile, foreign to its normal composition. Having had a chance of succeeding in this delicate research for a chlorate containing silica and sodium in the form of silicate of potassium and sodium, I subjected the purified chlorate to the action of heat in such a way as to form at the same time as the chloride:—

1st. The greatest possible quantity of perchlorate.

2nd. A quantity of perchlorate just sufficient to make the chloride necessary for determining its proportional combination with pure silver.

I will describe all these researches and the results at which I arrived as shortly as possible.

On the Methods used to Eliminate the Solid Foreign Bodies generally found in Commercial Chlorate of Potassium.

It follows, from sufficiently well-known facts, that chlorate of potassium purified by means of successive crystallisations to the point of no longer clouding a 10 per cent solution of silver may yet contain iron, manganese, copper, and silver, and always has in it some sodium, aluminium, calcium, and silicon.

Copper and silver are eliminated at once by the addition of a sufficient quantity of sulphide or hydrosulphide of potassium to a saturated solution of chlorate at 100°. At first almost all the iron and manganese remain in solution: they are only precipitated when one keeps the saline solution slightly boiling for from fifteen to thirty minutes; but in this state the liquid, which is alkaline, perceptibly attacks the porcelain or glass dish in which the operation is carried on.

The salt which crystallises out on *suddenly cooling* the filtered liquid from which the copper and silver have been thus eliminated is often slightly tinted pink. This colour disappears on carefully washing the salt with a solution containing 1·1000th part of hydrosulphide of potassium cooled nearly to zero, followed by a wash in pure iced water. When losing its colour, the chlorate loses the greater part of the iron and manganese, as well as the aluminium, sodium, calcium, and silicon.

On dissolving the salt thus obtained in pure boiling water, to saturation, and on adding to the solution a sufficient quantity of pure hydrosulphide of potassium to give it a strong alkaline reaction, one obtains, on suddenly chilling the *filtered* liquid, a white, powdery, crystalline chlorate, from which a wash in a solution containing one thousandth part of hydrosulphide of potassium, followed by a second wash in pure iced water, eliminates the remaining iron, manganese, and aluminium, but not all the silicon, sodium, and calcium contained in it. On repeating the dissolving, crystallisation, and washing a great number of times under the same conditions,—that is to say, in porcelain or glass dishes, and *in the presenee of air containing sodium and silicon*,—one can certainly diminish to a great extent the proportion of sodium, calcium, and silicon in the chlorate; but it appears to me that at the fourth treatment one reaches a limit at which the porcelain or glass dishes, and the surrounding air, supply as much silica, sodium, and calcium as the treatment suffices to eliminate.

After the third treatment one is therefore obliged to work in platinum vessels of a proper shape, and *in air enclosed and purified*. By acting thus, I have been able, by *six* successive crystallisations, of which the last *three* were in platinum, to obtain chlorate quite free from silicon, from all solid bodies whatever, and from sodium, provided this metal exists entirely in the raw chlorate in the form of silicate of sodium, as has been the case in all the samples of chlorate, save *one*, supplied to me. If, on the other hand, the sodium contained in it is partially in the form of sodium chlorate, there is a limit which one cannot *practically* pass, so long as one causes the separation of the silica by means of sulphide, or hydrosulphide of potassium, or potash, in addition to *carefully washing the crystals with alcohol*, in enclosed air.

I have tried this method of eliminating from chloride, sulphate, and nitrate of potassium, the silicon, aluminium, and calcium, which are nearly always met with in these compounds when purified by successive crystallisations.

With proper care, the elimination of these bodies is very easy, especially sulphate of potassium. After five successive crystallisations, of which the last three were effected in platinum and in air enclosed and purified, I have succeeded in obtaining a sulphate and a nitrate which, when warmed with just enough pure sal ammoniac, formed a chloride which volatilised without leaving a trace of solid residue. This study enabled me to prove that after the elimination of silicon, aluminium, and calcium, the sulphate, nitrate, and chloride still retain sodium, the chloride and nitrate in *very minute* quantities, the sulphate, on the other hand, in comparatively large quantities,—an evident proof that, in the compounds submitted to purification, the metal sodium existed respectively in the forms of sulphate, nitrate, and chloride. I repeat that the use of sulphide, hydrosulphide, and hydroxide, to catch the sodium, is only effective provided this metal is in the potassium salt exclusively as a silicate.*

I describe farther on, with necessary details, the preparation of the chlorate, perchlorate, and chloride of potassium used in my researches.

(To be continued).

ON THE TECHNICAL ANALYSIS OF CYANIDE WORKING SOLUTIONS.†

By W. BETTEL.

For some time past I have felt the need of some quick method of analysis which would in a reasonable time give the composition of working cyanide solutions, so that the chemist-in-charge, or the foreman, in a cyanide works, could trace to its source any irregularity in the working of such solutions with a view to its correction. After many fruitless trials I have pleasure in drawing your attention to some volumetric processes, which, although not all that could be desired, are still sufficiently accurate to be used for technical work, and have this advantage, that the work may be performed by men who have not had the advantage of a technical or scientific training. I do not lay claim to any novelty in this analytical process, it is merely pieced up from well known analytical methods and chemical reactions; but, nevertheless, I hope it will be useful to those of our members who have to examine cyanide solutions.

It is necessary to state at the outset that my remarks have reference to the MacArthur-Forrest working solutions containing zinc, an element which complicates the analysis in a truly surprising manner. Before dealing with the analysis proper, I will draw your attention to the peculiarities of a solution of the double cyanide of zinc and potassium, usually written K_2ZnCy_4. As is stated in works on chemistry, this cyanide is alkaline to indicators. Now here lies the peculiarity. To phenolphthalein the alkalinity, as tested by N/10 acid, is equal to 19·5 parts of cyanide of potassium out of a possible 130·2 parts. With methyl-orange as indicator, the whole of the metallic cyanide may be decomposed by N/10 acid, as under:—

$$K_2ZnCy_4+4HCl=ZnCl_2+2KCl+4HCy.$$

On titration with nitrate of silver solution the end-reaction is painfully indefinite. If caustic alkali in excess (a few c.c. normal soda) be added to a known quantity of potassic

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* I am certain that the principle involved in eliminating the silica and aluminium always contained in chlorate of potassium crystallised from pure water, by means of crystallisations made in water rendered alkaline by potash or hydrosulphide of potassium, is applicable to the elimination of the silica and aluminium contained in sulphate of sodium crystallised in pure water. By transforming sulphate thus purified, by means of chloride of ammonium, I have obtained chloride of sodium capable of being volatilised without leaving a trace of residue,—a thing I had not previously succeeded in doing. In future, one will be able to use the proportional combination with silver and chloride of sodium, and ascertain, without hypothesis, whether the atomic weight of silver and the molecular weight of chloride of sodium are integral multiples of that of hydrogen.—January, 1879.

† A Paper read before the Chemical and Metallurgical Society, Johannesburg, S.A.R., August, 1895.

zinc cyanide solution together with a few drops of potassic iodide, and standard silver solution added to opalescence, the reaction will indicate sharply the total cyanogen present in the double cyanide even in presence of ferrocyanides. If to a solution of potassic zinc cyanide be added a small quantity of ferrocyanide of potassium, and the silver solution added, the flocculent precipitate of what I suppose to be normal zinc ferrocyanide (Zn_2FeCy_6) appears, the end-reaction is fairly sharp, and indicates 19·5 parts of cyanide of potassium out of the actual molecular contents of 130·2 KCy. If, however, an excess of ferrocyanide be present, the flocculent precipitate does not appear, but in its place one gets an opalescence which speedily turns to a finely granular (sometimes slimy) precipitate of potassic zinc ferrocyanide, K_2Zn_3,Fe_2Cy_{12}. This introduces a personal equation into the analysis of such a solution, for if the silver solution be added rapidly the results are higher than if added drop by drop, as this ferrocyanide of zinc and potassium separates out slowly in dilute solutions alkaline or neutral to litmus paper.

This ferrocyanide is decomposed by—

(*a*) Potassic, sodic, or calcic cyanide, &c.;
(*b*) Potassic or sodic hydrate;
(*c*) Potassic or sodic carbonate;

as shown by the following equations:—

(*a*) $K_2Zn_3Fe_2Cy_{12}+12KCy=2K_4FeCy_6+3K_2ZnCy_4$.

(This equation is proved by mixing solutions of potassic zinc cyanide with one of potassic ferrocyanide, no precipitate occurs. Potassic zinc ferrocyanide is dissolved by cyanide solution).

(*b*) $K_2Zn_3Fe_2Cy_{12}+12KHO=$
$=2K_4FeCy_6+3ZnK_2O_2+6H_2O$.

(Potassic zinc ferrocyanide is readily dissolved by caustic alkali. If potassic (or sodic) zinc oxide in solution be added to potassic ferrocyanide no precipitate occurs even in absence of free alkali).

(*c*) $K_2Zn_3Fe_2Cy_{12}+12Na_2CO_3+6H_2O=$
$=2KNa_3FeCy_6+12NaHCO_3+3ZnNa_2O_2$.

(This is similar to the (*b*) reaction, with the difference that carbonates are converted into bicarbonates).

I will now draw your attention to the equations involved in the reaction previously described. As the percentage of alkalinity is definite, and consists of a portion of potassic cyanide loosely combined with zinc cyanide more firmly united with less cyanide than corresponds with K_2ZnCy_4, I venture to propose for provisional adoption the following equations representing the neutralising of K_2ZnCy_4 by acid and silver nitrate respectively:—

(*a*) $10K_2ZnCy_4+3HCl=$
$=3HCy+3KCl+(ZnCy_2)_{10},(KCy)_{17}$.

(*b*) $20K_2ZnCy_4+3AgNO_3=$
$=3KAgCy_2+3KNO_3+2[(ZnCy_2)_{10},(KCy)_{17}]$.

Here is a point for investigation, as to whether there is more than one definite crystallisable salt containing K+Zn+Cy, neutral to phenolphthalein, and soluble in water, or whether $ZnCy_2$ is soluble in a solution of K_2ZnCy_4 and produces neutrality to phenolphthalein.

For the estimation of free hydrocyanic acid I have made use of Siebold's ingenious method for estimating alkalis in carbonates and bicarbonates, by reversing the process, adding bicarbonate of soda, free from carbonate, to the solution to be titrated for hydrocyanic acid and free cyanide. This is the one instance where hydrocyanic acid turns carbonic acid out of its combinations, and as such is interesting.

$2KHCO_3+AgNO_3+2HCy=$
$=KAgCy_2+KNO_3+2CO_2+2H_2O$.

I will now proceed to describe the method of analysis.

1. *Free Cyanide.*—50 c.c. of solution is taken and titrated with silver nitrate to faint opalescence or first indication of a flocculent precipitate. This will indicate (if sufficient ferrocyanide be present to form a flocculent precipitate of zinc ferrocyanide) the free cyanide, and cyanide equal to 7·9 per cent of the potassic zinc cyanide present.

2. *Hydrocyanic Acid.*—To 50 c.c. of the solution add a solution of bicarbonate of potash or soda, free from carbonate or excess of carbonic acid. Titrate as for free cyanide. Deduct the first from the second result

$$=HCy\ 1\ \text{c.c.}\ AgNO_3=\frac{0·04145}{5}=0·00829\ \text{p. c.}\ HCy.$$

3. *Double Cyanides.*—Add excess of normal soda (caustic) to 50 c.c. of solution and a few drops of a 10 per cent solution of KI, titrate to opalescence with $AgNO_3$. This gives 1, 2, and 3. Deduct 1 and 2 = K_2ZnCy_4 as KCy less 7·9 per cent.

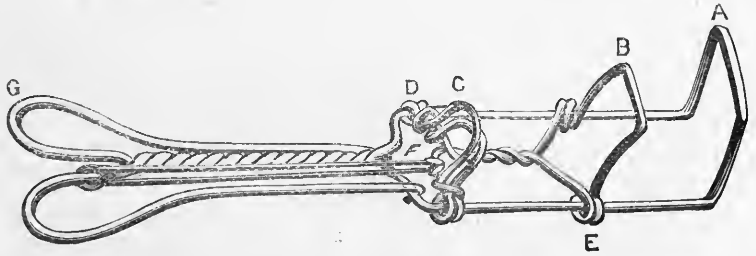
A correction is here introduced. The KCy found in 3 is calculated to K_2ZnCy_4. Factor: KCy (as K_2ZnCy_4) × 0·9493 = K_2ZnCy_4. Add to this 7·9 per cent of total, or for every 92·1 parts K_2ZnCy_4 add 7·9 parts. If this fraction, calculated back to KCy, be deducted from 1, we get the true free cyanide (calculated to KCy).

(To be continued).

A CONVENIENT FORM OF UNIVERSAL HAND-CLAMP.

By PETER T. AUSTEN and W. A. HORTON.

The various holders and hand-clamps used for holding test-tubes and smaller forms belong, as a rule, to two classes. The bite is effected either by a spring or by pressure exerted by the hand. The difficulty with the first class of holders is that the spring is often inconveniently strong for delicate tubes, and not strong enough for flasks. The second class often fails when long-continued holding is involved, as muscular pressure relaxes after a time.



The following little device was worked out to afford a convenient holder that should take from nothing up to a diameter of an inch and a half, and yet allow a grasp which corresponds to the weight of the object held, and also not tire the hand, no matter how long it is held.

The clutch B slides on the parallel bars E, and is slightly smaller than the counter-clutch A. This, with its curvature, allows it to grasp any object, no matter how small, that is placed between B and A. A double bearing, to insure ease of movement, is effected by winding the wire at D. The double arch C allows the thumb to press easily and comfortably against it, and act as a knee-joint. The swell G keeps the handle in the grasp, and the rubber strap F brings the travelling clutch back and opens the clamp as soon as the pressure is removed from C.

To use the apparatus, the handle is securely grasped and the end of the thumb is placed against C. On straightening the thumb, in the manner of a knee-joint, the object is tightly held between the clutches. The hand does not tire on continued holding, because the pressure is taken in a straight line on the bones of the thumb, and hence calls for so slight a muscular action as to be practically inappreciable.

The clamp is manufactured by Ermei and Amend.—*Journal of the American Chemical Society.*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1895.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Certificates were read for the first time in favour of Messrs. Joseph Edwin Alger Blyde, Nether House, Ranmoor, Sheffield; Arnold Eiloart, 2, Lansdowne Road, East Croydon; Walter Thomas Grice, 9, Dalhousie Square, Calcutta; James William Helps, 3, Tavistock Road, Croydon; Laurence W. Matthieson, 104, Grove Road, Bow, E.: Thomas Francis Rutter, The Huish School, Taunton; Arthur Philip Salt, Sunnyside, Pinner Road, Harrow; Amrita Lal Sircar, 51, Sankaritola, Calcutta; Benjamin Bernard Turner, 28, Lady Somerset Road, N.W.; and of Cass L. Kennicott, 4050, Ellis Arc, Chicago, Ill., U.S.A., approved by the Council under Bylaws 1, 3.

The President announced that a letter of thanks had been received from the French Academy, for the Address presented by the Society on the occasion of the centenary of the Academy, on October 25th.

Of the following papers those marked * were read:—

*135. "*The Influence of Temperature on Refractive Power, and on the Refraction Equivalents of Acetylacetone and of Ortho- and Para-toluidine.*" By W. H. Perkin, Ph.D., F.R.S.

The author points out that whilst he has proved that the refraction equivalent of certain compounds is subject to variation at different temperatures, and Brühl has observed the same fact, his numbers, and those obtained by Brühl, are not in agreement. In the case of acetylacetone, the toluidines, and other compounds, it is observed that the two sets of determinations agree closely for ordinary atmospheric temperatures, but at higher temperatures Brühl's numbers show an increase, whilst the author obtains smaller numbers at higher temperatures. The author has satisfied himself that the apparatus used by him (*Trans.*, 1892, 288) consisting of a hollow prism heated in an air-bath, furnishes uniform results, and by making observations with different specimens of material, he has proved that the differences between his numbers and Brühl's cannot be ascribed to impurity. Since the results for higher temperatures obtained by Nasini and Bernheimer, and by Kettler, using more or less independent methods, agree with the author's, he concludes that there must be some hitherto undiscovered error in the use of Brühl's refractometer at any temperature much above that of the atmosphere.

*136. "*The Evolution of Carbon Monoxide by Alkaline Pyrogallol Solution during Absorption of Oxygen.*" By Frank Clowes, D.Sc.

It has long been known that under certain conditions carbon monoxide is evolved during the absorption of oxygen by alkaline pyrogallol. When a solution, 100 c.c. of which contains 10 grms. of pyrogallol and 24 grms. of potassium hydroxide, is used for the absorption of oxygen, it evolves no carbon monoxide until the percentage of oxygen in the gaseous mixture exceeds 28. The carbon monoxide evolved, however, increases in amount as the percentage of oxygen rises above that limit, until the carbon monoxide finally reaches about 6 per cent of the volume of oxygen absorbed.

The process of estimation of oxygen is rendered perfectly accurate if the carbon monoxide which has been produced during the absorption is removed by means of cuprous chloride solution before the reading is taken.

Experiments with pyrogallol solution containing larger proportions of potassium hydroxide than that given above proved that the evolution of carbon monoxide may be entirely prevented under all conditions if the potassium hydroxide is present in sufficiently large proportion.

A solution, 100 c.c. of which contains 10 grms. of pyrogallol, and 120 grms. of potassium hydrate, proved perfectly satisfactory in this respect; the weight of pyrogallol may be reduced to 5 grms. in this solution.

A solution containing 18 per cent of quinol (hydroquinone) and 24 per cent of potassium hydroxide absorbed oxygen slowly, but the absorption was complete, and no carbon monoxide was evolved.

It is therefore evident that serious error may arise in estimating the proportion of oxygen present in a mixture containing only small proportions of other gases, unless the absorbent pyrogallol solution is prepared of suitable strength, or unless the absorption of oxygen is followed by the treatment of the residual gas with cuprous chloride solution.

*137. "*The Composition of the Limiting Explosive Mixtures of various Combustible Gases with Air.*" By Frank Clowes, D.Sc.

A series of experiments were made with mixtures in varying proportions of each combustible gas with air. A flame was brought into contact with each mixture, sometimes above and sometimes below, and it was noted whether the mixture burnt back independently of the external air. For each combustible gas there was thus obtained a lower percentage below which the mixture would not burn independently, and a higher percentage, above which the gas burnt independently only when it was supplied with more air.

The limiting percentages were as follows:—For methane, 5 and 13; for hydrogen, 5 and 72; for carbon monoxide, 13 and 75; for ethylene, 4 and 22; for water-gas, 9 and 55; for coal-gas, 5 and 28.

It was also proved that many mixtures which were outside but close to the above limits, and which could not be fired from above could be fired from below.

Hence it is inferred:—

1. That the limiting explosive mixtures for different combustible gases vary widely.
2. That methane shows the narrowest limits, hydrogen the widest limits.
3. That the risk of a mixture being fired explosively increases with the different gases in the following order:—Methane, ethylene, coal-gas, water-gas, carbon monoxide, hydrogen.
4. That the risk of explosion is greater when the mixture is kindled from below than when it is kindled from above.

Discussion.

Mr. Bennett H. Brough considered that it would have been a valuable addition to Professor Clowes's investigations if the action of other methods of firing had been tried. For it had to be remembered that colliery explosions were sometimes due to inflammation by sparks such as were produced by picks. Some interesting experiments had recently been made in the Moravian Ostrau coalfield in Austria with an apparatus for testing the liability of gaseous mixtures to inflammation in that way. A wheel was mounted on a vertical axis inside a casing, which was hermetically sealed and provided with a large removable cover. Definite proportions of gas were introduced and mixed with the air by revolving the wheel. An iron bar sliding through the casing was brought against the revolving wheel, and in case of an explosion the cover, which was secured by a chain, was blown off without further damage.

*138. "*Note on the Estimation of Butyric Acid.*" By W. H. Wilcox, B.Sc.

In the estimation of butyric acid in the presence of acetic and formic acids, the acids were neutralised by a known excess of calcium carbonate. Hydrochloric acid was added in sufficient amount to neutralise the free calcium carbonate and to liberate the butyric acid from the calcium salt. The solution was distilled, and when the greater part had passed over, steam was passed through the liquid as long as the distillate continued acid. The distillate, which contained the butyric acid, was boiled with pure barium carbonate, the solution filtered, and evaporated to dryness.

It was found that when dried at 100° C., the salt did did not attain a constant weight even after it had been heated for several weeks, diminutions of about 2 m.grms. (with 1 to 2 grms. of salt) occurring after heat had been applied for three hours. This loss of weight did not occur at and below 80°.

Some barium butyrate was prepared, and was found to lose weight in a similar manner. At 90—100° C. losses of about 2 m.grms. occurred with three hours heating of 1·5 grms. of salt, and even at 85° C. loss of weight occurred on continued heating. When the salt was kept at 80° C., however, it speedily arrived at a constant weight, which was not altered by continued heating.

These results show that in the estimation of mixtures of the volatile fatty acids, when butyric acid is present, the fraction of salts containing the butyrate must be dried at a temperature not exceeding 80° C.; if this temperature is exceeded, loss of weight occurs owing to the decomposition of the butyrate.

139. "*Some Derivatives of Anthraquinone.*" By Edward Schunck, Ph.D., F.R.S., and Leon Marchlewski, Ph.D.

The authors have prepared the three hitherto unknown methyl purpuroxanthins. One of them was obtained by condensation of *o*-toluic acid with *m*-hydroxybenzoic acid. It crystallises in orange-coloured needles (m. p. 246°). Its diacetyl derivative is nearly colourless (m. p. 195°).

The other two methylpurpuroxanthins were obtained by condensation of *m*-toluic acid and *m*-hydroxybenzoic acid. The mixture of methylpurpuroxanthins produced, yielded two distinct compounds by fractional crystallisation from a mixture of alcohol and benzene. The constitution of these compounds was determined by studying the products of their oxidation. The more soluble one gave, on treatment with nitric acid, trimellitic acid, while the other one gave, on similar treatment, hemimellitic acid.

The authors point out that the constitutional formulæ proposed by them (*Trans.*, 1894, 186) for the ethers of alizarin are supported by the work of Lagodzinski (*Ber.*, 1895, 1427), who obtained a monomethyl ether of alizarin by the condensation of hemipinic acid with benzoic acid.

The authors give a more precise account of the ethers of anthraquinoneoxime, mentioned by them in a preliminary paper previously published (*Ber.*, 1894, 2125). The methyl ether melts at 147°, the ethyl ether at 97°, and the benzyl ether at 82°.

140. "*Efflorescence of Double Ferrous Aluminium Sulphate on Bricks exposed to Sulphur Dioxide.*" By David Paterson.

The author has analysed the efflorescence which appears on bricks composing chambers in which wool is bleached with sulphur dioxide. Four analyses were made, and the results agree well with the percentages required by the formula $Al_2(SO_4)_3,FeSO_4,24H_2O$. The salt forms white fibrous crystalline masses resembling asbestos in appearance. It is evidently identical with the salt often found in volcanic regions, and the author's analyses agree well with those made by Forchammer of a specimen obtained from Iceland.

Collective Index of the Transactions, Abstracts, and Proceedings of the Chemical Society.

Volume II., 1873 to 1882. Volume III., 1883 to 1892.

The Council, having determined to publish a Collective Index of their publications from 1873 to 1892 inclusive, will issue copies to Fellows who may notify their wish to receive them. Both volumes will be sent to those who were Fellows of the Society before the end of 1882. Volume III. will be sent to Fellows who have joined the Society between 1st January, 1883, and 31st December, 1892. Fellows who are ineligible to receive copies *gratis*, and those who may have neglected to apply for them within the prescribed period, may obtain them by purchase at a price to be hereafter fixed. Fellows who desire the Index should notify their wish by letter, enclosing 1/- for cost of distribution, &c., to the Assistant-Secretary, Mr. Robert Steele, Chemical Society, Burlington House, W., before 31st December, 1895. For Fellows resident abroad, who should remit 2/-, which may be paid with their annual contribution, the time will be extended to March 1st, 1896.

A few copies of Vol. I. (1841—72) can still be obtained, price 3/- post free.

Research Fund.

A meeting of the Research Fund Committee will be held in December.

IMPERIAL ACADEMY OF SCIENCES OF VIENNA.

Session of the Mathematical and Natural Science Section, of October 24th, 1895.

"*On the Red Spectrum of Argon.*" By Dr. J. M. Eder and Dr. E. Valenta.

By the kindness of Lord Rayleigh we obtained a specimen of argon gas which had been carefully introduced into vacuum tubes by Herr Goetze, of Leipzig. The pressure in the tubes which we used in our experiments was from 1 to 3 m.m. For the spectroscopic analysis of the argon we used a concave grating having a radius of curvature of ¾ metre, employing the photographic method. We examined the red and the blue spectrum obtained by working according to the directions of Mr. Crookes, with weak sparks without Leyden jars, or with sparks from the jars.

For the red spectrum of argon we obtained the numbers quoted below. The lines marked with asterisks in the author's tables are present also in the blue spectrum of argon. The other lines are peculiar to the red argon spectrum. The especially characteristic lines of the red argon spectrum are:— λ 4628·56, 4596·22, 4522·49, 4510·85, 4300·18, 4272·27, 4259·42, 4251·25; especially the group 4200·76, 4198·42, 4198·07, 4164·36, 4158·63; and further, 4044·56, 3949·13, 3834·83. Further measurements will appear in the *Transactions of the Imperial Academy*. It must also be remarked that the red argon spectrum is well resolved when the double line $\left\{\begin{matrix}4191\cdot15\\4190\cdot75\end{matrix}\right.$ appears clearly separated.

If the blue and the red argon spectrum belong to two elements, which is by no means improbable, the above lines would be the main characteristic lines of one of them.

NOTICES OF BOOKS.

A Handbook of Industrial Organic Chemistry: adapted for the Use of Manufacturers, Chemists, and all interested in the Application of Organic Materials in the Industrial Arts. By Samuel P. Sadtler, Ph.D., F.C.S., Professor of Chemistry in the Philadelphia College of Pharmacy, and in the Franklin Institute of the State of Pennsylvania, &c. Second and Revised Edition. 8vo., pp. 537. Philadelphia: J. B. Lippincott Company. London: 10, Henrietta Street, Covent Garden. 1895.

Prof. Sadtler admits that there is, on the one hand, no lack of technological manuals for separate chemical industries, such, *e.g.*, as tanning and dyeing; and, on the other hand, of encyclopædic works embracing the entire compass of the chemical arts, but that there is a scarcity of works which attempt to give, within the compass of a single volume, a general view of the various industries based upon the applications of chemistry to the arts." The reason of this rarity is not difficult to find. The chemical industries are now so numerous and so elaborate that to give in a single volume anything beyond a mere sketch of each, of comparatively little practical value, is indeed an arduous task. To escape this difficulty the author confines himself in the volume before us to the organic arts, and promises to give an account of the inorganic chemical industries in a future volume. This expedient certainly reduces the bulk of the matter to be dealt with, but it encounters the difficulty that there is no hard and fast boundary line between the organic and inorganic chemical arts.

If we turn to the subjects discussed in this volume—such as tanning, soap-making, dyeing, bleaching, and tissue-printing—we find that they are at once organic and inorganic. The same must be said of the manufacture of chemical manures, of painters' colours, and writing inks, which are not mentioned in the work before us, and each of which would likewise overstride the boundary line. Again, when the companion volume appears the work will no longer give a view of the chemical industries within the bounds of a single volume.

If we might suggest, a principle of division preferable to that of "organic and inorganic" might be found, though it would not be easy to find scientific names for the two respective groups of industries. Let us suppose, by way of explanation, that on visiting some strange town we were to enquire what chemical works there were in the district. We should then feel startled if we were told of a number of dairies, bake-houses, breweries, and sugar-works. Yet the processes carried on in these establishments are unquestionably chemical. Still we feel, however difficult it may be to put the distinction in words, that they do not belong in the same category as bleach-works, soap-works, or tanneries.

Passing from questions of arrangement to the subject-matter itself, we must congratulate Dr. Sadtler on the rare felicity with which he has condensed into so small a space so large an amount of valuable matter. Oversights and errors are indeed rare. We note merely a passage which seems to convey the impression that indigo is always applied to textile goods by means of the cold vat, whilst in fact the warm vats are chiefly used in woollen-dyeing.

A most valuable feature of this book is the biographical department subjoined to each section. The student is thus furnished with a master-key which opens to him all the details of technical chemistry.

Hints on the Teaching of Elementary Chemistry in Schools and Science Classes. By W. A. Tilden, D.Sc., F.R.S. Crown 8vo., pp. 76. London and New York: Longmans, Green, and Co. 1895.

Manuals of elementary chemistry are far from rare,—too plentiful, indeed, as we are sometimes tempted to think. But the little work before us is exceptional in its character. It is addressed not to students, but to teachers, and thoroughly good lessons does it convey. Pity, though, we must add with bated breath, that any teacher of chemistry, or of any science, should need such hints.

In the first sentence of the Preface Dr. Tilden rejoices over the issue of a new "Syllabus." It may be a very important advance in the teaching of chemistry, as giving more scope to the discretion of the teacher. But there would be still greater room for congratulation if the new "Syllabus" were the last of the race! It is appropriately urged that the teacher should devote some part of his time to extending and consolidating his own knowledge. Should he need any such reminder? We find a denunciation of the "crammer," but due reflection will tell us that this unlovely being is a bye-product of examinationism.

We are inclined to agree with Prof. Tilden when he expresses the opinion that the study of chemistry, when rightly taught, is the best means of cultivating the faculty of observation. The general incapacity of distinguishing objects unless they differ markedly in size or colour is duly regretted. This incapacity is, we fear, most striking in those who have "enjoyed" a classical education.

The author points out that chemistry cannot be learnt by reading alone. The eye and the hand must first be trained. One of the dangers of working from text-books is that "the student imbibes the idea that the subject is complete, rounded off, and finished, and that he sees no room for further inquiry."

It will not, we hope, be deemed irrelevant if we point out the fatal blow which the examinational system has just received. In the Chinese Empire, for ages, all statesmen, generals, judges, and magistrates have been selected by competitive examination. The outcome has been the collapse which the world has just witnessed. Intellectually and morally the examinee has been weighed in the balance and found utterly wanting.

Simple Methods for Detecting Food Adulteration. By John A. Bower. With 36 Illustrations. Published under the Direction of the General Literature and Education Committee. Small post 8vo., pp. 118. London: Society for Promoting Christian Knowledge. 1895.

Time was when the publications of the Society for Promoting Christian Knowledge were spoken of with scanty respect, but the number of valuable works by writers of acknowledged merit which have appeared with the imprimatur of the Society have done away with such an unjustifiable feeling. Mr. Bower's work is not intended as a guide for the student or a work of reference for the professional analyst, but it is calculated to guard the general public against frauds which affect their pocket, if not their health.

The author concludes that "adulteration is decidedly on the decrease," and again, that "our food is not adulterated to an alarming extent." Yet he qualifies these disclaimers by the admission that, as recently as the year 1891, "about 12 per cent of all the food sold in this country was adulterated," that coffee is sometimes sophisticated "to the amount of 75 per cent," that milk may contain from 20 to 30 per cent of added water. Now these facts show, we submit, that adulteration is still carried on to an "alarming extent," and that the apathy of the public—the persons thus defrauded—is in itself almost criminal.

Mr. Bower quotes several clauses of the "Sale of Food and Drugs Act," which has many deficiencies. Thus, in the case of coffee, to sell mixtures of coffee and chicory not conspicuously labelled as such is undoubtedly punishable; but if an enterprising tradesman wishes to sell chicory at the price of coffee, and of course to people who prefer coffee and do not want chicory, he needs merely sell his mixture as "French coffee," or "Coffee as in France," and he escapes the provisions of the Act! It would be easy to put a stop to this disgraceful fraud. Until lately it was practicable to avoid this fraud by always buying coffee unground; but criminal ingenuity now manufactures spurious coffee-beans, as well as spurious peppercorns, nutmegs, and, we believe, gall-nuts. Such devices require a punishment heavier than fines. It should be enacted that any person designing, constructing, vending, offering for sale, or using any machine, mould, stamp, or die for making up any powder, paste, or pulp into the shape of any berry, nut, or seed used in food or medicine, or selling any products thus moulded, shall on conviction be sentenced to imprisonment for not less than six months.

A fraud in the sugar-trade has escaped the author's notice. Continental growers of beet-sugars colour some of their unrefined product with yellow coal-tar dyes, and export the precious mess to England under the name of Demerara sugar! Thus they kill two birds with one stone. They sell their rank-tasting produce for more than it is fairly worth, and they damage the reputation of genuine Demerara sugars. Even the bees and the wasps know the difference between beet- and cane-sugars, and reject the former if the latter is accessible.

We believe that this work, addressed as it is to the general public, will aid in the necessary task of creating a healthy hostility to sophistication and sophisticators.

An Exercise Book of Elementary Practical Physics. By Richard A. Gregory, F.R.A.S. (Oxford University Extension Lecturer). Pp. 172. London and New York: Macmillan and Co. 1895.

This book, we are told on the title-page, is intended for "organised Science schools under the Department of Science and Art, evening continuation-schools and elementary day-schools." We further learn that it has been "arranged according to the Head-masters' Association Syllabus of Practical Physics." The table of contents reproduces the Head-masters' Association Syllabus, with a few changes and additions.

The reader will perhaps find the term "physics" here used in a sense which he scarcely expected.

Light, electricity, and magnetism are not touched upon at all, and heat very slightly. The main subject of the work is mechanics, with meteorology. What the book undertakes to teach, however, is well taught, and those who have made use of it, whether teachers or students, will not find that they have anything to unteach or unlearn.

Franklin Institute: Announcement and Programme of Lectures, 1895—1896. No. 15, South Seventh Street, Philadelphia.

The organisation of this Society is rather complex. It has a board of trustees; a staff of officers and managers; a board of management; two curators; four professors for the respective departments of mechanics, physics, chemistry, and economic geology; and a number of committees. There are five classes of members, viz., contributing members, stockholders, life members, permanent members, and non-resident members.

Among the lectures in the ensuing session the following are, from our point of view, the most interesting:—"Metallurgical and other Features of Japanese Swords," by Mr. B. S. Lyman; "Recent Improvements in the Chemical Treatment of Fibres and Fabrics," by L. J. Matos; "Modern Theories of Fermentation," by Dr. F. Wyatt; "Electro-metallurgy of Aluminium," by Dr. J. W. Richards; "Some Recent Work in Molecular Physics," by Prof. R. A. Fessenden; "What constitutes a Good and Safe Drinking Water?" by T. M. Drown, M.D., LL.D., of Lehigh University.

Craft Instruction: Photography and Process.

This pamphlet, which is issued at the Polytechnic Institution, W., bears no author's name. It consists of an elaborate prospectus of the photographic department of the Polytechnic Institution, which is now in its fourteenth session. There are also the advertisements of a number of manufacturers of, and dealers in, cameras, lenses for photography, and accessory appliances.

CORRESPONDENCE.

ON THE PLACE OF HELIUM IN THE CLASSIFICATION OF ELEMENTARY SUBSTANCES.

To the Editor of the Chemical News.

Sir,—In the report of the recent meeting of the Physical Society of November 22nd in the Chemical News (vol. lxxii., p. 266), in which the investigations of Profs. Runge and Paschen on the spectrum of the new gases from clèveite are referred to, I observe that Dr. Gladstone places these gases between hydrogen and lithium, in order that they may come into a classification based on a supposed periodicity of chemical properties when the elements are arranged in seriatim order of their atomic weights. I have shown elsewhere why the new gases cannot be allocated to the places assigned to them by Dr. Gladstone, and have to express my surprise that this chemist should, by loose arithmetic and still looser assertions, endeavour to controvert the reasons I have given for placing the new gases at the head of the second and third series of my table of elementary substances. The mis-statements to which I take exception as hindering the progress of chemical science are—

(1). That the successive differences between the atomic weights of adjacent members of the metals in the first group in Mendeleeff's table showed that these differences increased as we go downward.

And (2). "That if the new gases have atomic weights of, say, 2 and 4, we should have for these differences 2, 2, 3, 16, 16, 26, &c., instead of 6, 16, 16, &c., as at present."

Now the incorrectness of these alleged increasing differences in the atomic weights will be at once apparent from a simple inspection of the first group in Mendeleeff's table, in which I have included Dr. Gladstone's numbers for the new gases.

		Diff.
H	= 1	
		− 1
Hl_1	= 2	
		− 2
Hl_2	= 4	
		− 3
Li	= 7	
		− 16
Na	= 23	
		− 16
K	= 39	
		− 24
Cu	= 63	
		− 22
Rb	= 85	
		− 23
Ag	= 108	
		− 25
Cs	= 133	

It will, moreover, be evident that, even if the successive differences between the atomic weights in the first group increased as Dr. Gladstone alleges, the numerical relation would afford no ground for placing the new gases above lithium, as they might for the same reason be placed above the typical members of any other group in Mendeleeff's table.

In my paper on "Some New Relations of the Atomic Weights" published in the Chemical News (vol. xxxviii., p. 66, &c.), I have shown that in the first group or series H_n all the atomic weights after Na have a constant difference of 23; and in the second series H_{2n} a common difference, after Mg, of 24. As these series are of considerable interest at the present time, I will, by your permission, reproduce the part of my table containing them, with the addition of the accepted atomic weights for the purpose of comparison.

1.	$+\mathrm{H}n-$		$+\mathrm{H}2n-$	
2.	Li = 7 .. .. 7*		Gl = 8 .. .. 9·2	
3.	Na = 23 23	F = 19 19	Mg = 24 24	O = 16 16
4.	K = 39 39	Cl = 35 .. .. 35·5	Ca = 40 40	S = 32 32
5.	Cu = 62 .. .. 63·3		Zn = 64 65	
6.	Rb = 85 85	Br = 81 80	Sr = 88 .. .. 87·5	Se = 80 79
7.	Ag = 108 108		Cd = 112 112	
8.	Cs = 131 132	I = 127 127	Ba = 136 137	Te = 128 128
9.	*x* = 154		*x* = 160	
10.	*x* = 177		*x* = 184	
11.	Hg = 200 200		Po = 208 207	

* Accepted atomic weights.

In this table it will also be seen that the negative elements of the first and second series after Cl and S have constant differences of 46 and 48 respectively, or double the differences of the atomic weights of the members of each adjoining positive series of elements. The common difference of 16 of the atomic weights in the table above K, Cl, Ca, and S are equally interesting and significant. I have already, in the paper referred to, directed attention to the common difference of 4 between the halogens and the alkaline metals in homologous positions, and the common difference of 8 between the oxygen series and the alkaline-earth metals in similar positions: while the fact that the theoretic atomic weights of the members of the four series, when taken together, differ by less than half of one per cent from the actual determinations establishes the law of the multiple relations and constant differences of the atomic weights of these series on a solid and immutable basis—the heritage of chemical science for all time.—I am, &c.,

Henry Wilde.

December 3, 1895.

CHEMICAL EDUCATION.

To the Editor of the Chemical News.

Sir,—Your correspondent "W. A. D." has certainly pointed out one of the causes why chemical research is not more abundant in Britain, and why many of our chemical arts are declining. The evil factor is the exorbitant price of alcohol, a reagent constantly required both in research and in manufactures as far as organic products are concerned. Methylated spirit did, indeed, to a great extent lighten the burdens of the chemist, but, *suadente diavolo*, this concession has now been stultified by the excise ukase demanding the further addition of mineral naphtha. Whether this stipulation has been made in the fancied interest of the revenue or of "temperance" it has been decided without any regard to the interests of Science or Industry. If it is necessary to render methylated spirit absolutely undrinkable the addition of a mere trace of Dippel's animal oil, as the German Government allows for alcohol to be used in the colour industries, would have met the difficulty.

It is perfectly true that a methylated spirit may be obtained free from mineral naphtha, by dint of a sufficient unrolling of red tape, and with the pleasant condition of rendering our laboratories or works open to the visits of the exciseman. The only marvel is not that the Government took a foolish step, but that the interests threatened did not at once rise on the defensive and insist on the withdrawal of the oppressive regulation.—I am, &c.,

W. S.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 21, November 18, 1895.

On an Element, probably Novel, existing in the Terbias.—Lecoq de Boisbaudran.—I solicit the Academy for permission to submit a paper which I have written formerly (May 3, 1886) on an absorption-band observed in certain portions of a fractionation of terbia, and which I believe to be characteristic of a peculiar element. I had hoped to continue the study of this band, but having successively used up my samples of terbia in various experiments, there remains so little of this earth that further fractionations have become impossible. My memorandum of 1886 is:—My present terbia is an earth of a deep reddish brown, the hydrochloric solution of which gives only a weak absorption spectrum, entirely composed of the bands of dysprosium, and of a band which appears to belong to a new element. This is a brief description of this band:—Micrometer, 140·8; λ, 487·7. Observations: Apparent medium of a nebulous band, a little more indistinct on the left than on the right. Breadth, from 2 to 2½ degrees of the micrometer; intensity, moderate. The band 140·8 does not appear to belong to Ta_2O_3, since it is seen at least as strongly in earth of a little brightet colouration, as in my purest terbia. It does certainly nor belong to dysprosium, being more or less strong than the band Dy β 148·3, according to the products examined. Provisionally I shall name the earth producing the band 140·8 ($\lambda = 487·7$) Z δ.

Origin of Atmospheric Oxygen.—Dr. T. L. Phipson. The author's views on this subject have already appeared in the Chemical News for the years 1893 and 1894.

Synthesis of Methyleugenol. Constitution of Eugenol—Ch. Moureu.—The author causes allyl iodide, $ICH_2—CH=CH_2$, to react upon veratrol in presence of zinc powder. The method admits of generalisation, and he intends to apply it to the synthesis of safrol, anethol, and estragol.

Cholesterines of the Cryptogams.—E. Gérard.—The chloresterines existing in the lower plants all belong to the group of ergosterine.

Distribution of Pectase in the Vegetable Kingdom, and on the Preparation of this Diastase.—G. Bertrand and A. Mallevre.—Pectase may be considered as occurring universally in green plants. It is especially abundant in the leaves, from which it is extended into the other organs. The richness of certain leaves in pectase allows us to realise for the first time the proportion of this ferment.

Retting of Flax, and on its Microbian Agent.—S. Winogradsky.—The organism in question is relatively large, forming spores in the terminal swellings (tadpole shape). Its joints are from 10 μ to 15 μ in length by 0·8 μ in thickness. The retting of flax may be considered as a pectic fermentation in the microbiological sense of the word.

Zeitschrift für Anorganische Chemie,
Vol. viii., Parts 4 and 5.

The late Professor G. Krüss.—A faithful record of the life and activity of the late founder and editor of the *Zeitschrift für Anorganische Chemie*, with a bibliography of his memoirs and publications, truly wonderful considering his early death.

Revision of the Atomic Weight of Strontium.—Th. W. Richards.—Already inserted.

Determination of Carbon in Iron.—F. Foerster.—Among the procedures which give trustworthy values for the determination of carbon in iron, the copper-ammonium chloride can be executed with the simplest appliances at hand in every laboratory, and does not make such demands on the experience of the analyst as does, *e.g.*, the chlorine process. Sometimes its general applicability is interfered with by the fact that some sorts of wrought irons, especially tungsten-steels if in contact with a quite neutral solution of copper-ammonium chloride, give a violent escape of gaseous hydrocarbons. In such cases the author, instead of a solution of copper-ammonium chloride, uses a solution of copper-ammonium oxalate. This is obtained by mixing a 10 per cent solution of copper sulphate with a solution of ammonium oxalate saturated in heat until the initial precipitate is re-dissolved. Of this solution, 250 c.c. are poured upon 2 to 3 grms. of the tungsten-steel to be analysed, and heated together in the water-bath at 80° for five hours. Copper separates out, and the liquid takes a green colour. It is decanted away from the residue, the copper is dissolved away with a solution of copper-ammonium chloride, when the residual carbonaceous substance, after filtration and drying, is burnt in a current of oxygen.

Atomic Weights of Nickel and Cobalt.—Clemens Winkler.—Already inserted.

Acidimetric Determination of Molybdic Acid.—Karl Seubert and W. Pollard.—In the summer of 1890, by occasion of the analysis of a hydrated molybdic acid which had crystallised out of a molybdenum solution, we made the experiment of determining the proportion of free acid in the precipitate by supersaturation with soda-lye and titrating back with hydrochloric acid, using phenolphthalein as indicator. The results were satisfactory. Various indicators were used, but only phenolphthalein and litmus proved satisfactory. The lye must be carefully prepared, and should be preserved from carbonic acid.

Quantitative Separation of Metals by Hydrogen Peroxide in Alkaline Solutions.—P. Jannasch and A. Röttgen.

Action of Heat upon Carbon Sulphide.—Henryk Arctowski.—By the action of heat upon the vapour of carbon sulphide, the author obtains the substance which occasions the unpleasant odour of carbon disulphide. It is probably the same as Bela v. Langyel's carbon sesquisulphide.

New Nitroso-compounds of Iron.—K. A. Hofmann and O. F. Wiede.—The authors have succeeded in obtaining well-characterised salts of an acid of the formula $Fe(NO)_2SSO_2OH$.

Cause of Osmotic Pressure and of Ionisation (Electrolytic Dissociation).—J. Traube.—A continuation of a very extensive memoir, not suitable for abstraction.

Determinations of the Molecular Weights of Solids, Liquids, and Solutions.—J. Traube.—Not capable of useful abridgment.

Action of Dry Hydrogen Chloride upon Serpentine.—R. Brauns.—This paper is chiefly a critique of the researches of Clarke and Schneider. It is concluded that the hydrochloric gas employed by those chemists was mixed with traces of water, and hence could not be regarded as sufficiently dry. It was rendered capable of reaction by the presence of watery vapour, and has thus occasioned the decomposition of the magnesium silicate. Water was formed by the decomposition of these silicates, and promoted further decomposition. It cannot be concluded from the occurrence of the reaction in hydrogenous minerals in what manner their hydrogen is combined. The number of the Mg—OH groups cannot be inferred from the quantity of the chlorides formed. Hence the experiments of Clarke and Schneider—in as far as they refer to the action of hydrogen chloride upon silicates—are not adapted to yield a decision on the constitution of the silicates examined.

Simple Method of General Applicability for the Determination of Water in Silicates.—P. Jannasch and P. Weingarten.—This paper requires the accompanying figure.

The Chemical Composition and Constitution of Vesuvian.—P. Jannasch and P. Weingarten.—A tabular view of the analytical composition of vesuvian from various localities, distinguishing the specimens containing fluorine and those from that halogen.

Opening Up Silicates by the use of Pure Lead Carbonate.—P. Jannasch.

Crystalline Copper Ferrocyanides.—J. Messar.—A full account of the formation, composition, and properties of sodium cuproferrocyanide, sodium cuprocyanide, potassium cuproferrocyanide, ammonium cuproferrocyanide, ammonium cupriferricyanide, magnesium cuproferrocyanide, magnesium cupriferrocyanide, calcium cupriferrocyanide, strontium cupriferrocyanide, barium cupriferrocyanide, and ferrocyancuprammonium.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxi., No. 3.

This issue contains no chemical matter.

MISCELLANEOUS.

Salters' Company's Research Fellowship. — The Executive Committee of the City and Guilds of London Institute are inviting applications for the appointment to the Salters' Company's Research Fellowship for the ensuing year. The Fellowship was founded by the Salters' Company for the encouragement of higher research in chemistry in its relation to manufactures, and particulars of the scheme under which the award is made may be had on application to the Honorary Secretary, at the Head Office of the Institute, Gresham College, Basinghall Street, E.C. The results of the researches by Dr. Martin O. Forster, the Salters' Research Fellow for the current year, at the Institute's Central Technical College, were communicated to the Chemical Society at its last meeting.

Mercury-thymolo-acetate.— E. Merck. — The Chemical News not being a medical organ, we cannot give instruction for the use of any medicine, especially one of the "proprietary" class. The only point we can notice is that the bacillus of tuberculosis is very similar to that of syphilis.

MEETINGS FOR THE WEEK.

Monday, 19th.—Society of Arts, 8. "Mechanical Road Carriages," by H. Worby Beaumont, M. Inst.C.E. (Cantor Lectures).
Tuesday, 17th.—Institute of Civil Engineers, 8.
—— Pathological, 8 30,
—— Photographic, 8.
—— Society of Arts, 4.30. "Jamaica in the Past and Present," by Frank Cundall.
Wednesday, 18th,—Society of Arts, 8. "Machines for Composing Letter-press Printing Surfaces," by John Southward.
—— British Astronomical, 5.
—— Meteorological, 7.30.
—— Geological, 8.
—— Microscopical, 8.
Thursday, 19th.—Chemical, 8. "Liquefaction of Air" and "Properties of Liquid Air," by Prof. Dewar, F.R.S. Discussion on "The Constitution of Terpenes and Camphor," "Derivatives of Dimethylaniline," by Miss Evans, B.Sc.
Friday, 20th.—Quekett Club, 8.

TO CORRESPONDENTS.

C. E. B.—It is doubtful whether the propounder of the question whether F should rank along with Cl, Br, and I could give a strictly scientific answer. He asks why is it not "*usually* included in that group?" He does not say "naturally" or "legitimately." Fluorine was till very lately an element of unknown properties, and hence it was commonly excluded from the group of the halogens. Its chief difference is that its oxide has not yet been obtained.

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The Court of the Salters' Company having placed at the disposal of the City and Guilds of London Institute a Grant of £150 a Year for founding one or more Fellowships for the encouragement of Higher Research in Chemistry in its relations to Manufactures, the Executive Committee of the Institute are prepared to receive applications from candidates for appointment.

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A Copy of the Scheme, giving particulars of tenure, &c., under which the Fellowships will be awarded, may be had on application at the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C.

JOHN WATNEY, Honorary Secretary.

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PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN that Heinrich Baum, of No. 28, Forsthausstrasse, Frankfort-on-the Main, in the Empire of Germany, has applied for leave to amend the Specification of the Letters Patent No. 12942 of 1893, for "Improvements in the Manufacture of Ortho-halogen-phenol, and in the Production of Pyrocatechine therefrom."

Particulars of the proposed Amendments were set forth in the Illustrated Official Journal (Patents) issued on the 4th December, 1895.

Any person or persons may give notice of opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

(Signed) H. READER LACK,
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THE CHEMICAL NEWS.

VOL. LXXII., No. 1882.

EXAMINATION OF GASES FROM CERTAIN MINERAL WATERS.*

By ALEXANDER KELLAS, B.Sc., and
WILLIAM RAMSAY, Ph.D., F.R.S.

A SAMPLE of gas of an inflammable nature, sent to Mr. Crookes by Mr. C. Lowthian Bell, of Middlesbrough, from "Allhusen's Well," was sent on to us to be tested for argon. The usual constituents, nitrogen, hydrocarbons, &c., were removed by the usual absorbents, magnesium, copper oxide, &c., and finally by sparking with oxygen over caustic soda. The only noticeable feature was the great difficulty in removing the hydrocarbon, which for long resisted the action of red-hot copper oxide. The circulation had to be continued for two days before absorption was nearly complete. In one case (Kellas) 555 c.c. of gas gave 2 c.c. of residue, and in another (Ramsay) 950 c.c. gave 4·5 c.c. This corresponds to about 0·4 per cent of indifferent gas. The first portion was unfortunately lost, but the spectrum of the second portion was carefully compared with that of argon, and the lines were all found to be coincident. No new lines appeared, nor was any helium yellow visible.

An incombustible gas from another well at the same place was also tested, and was found to contain 0·5 per cent of argon (Kellas).

Some gas from a boiling spring near Reykjavik, Iceland, was collected last autumn (Ramsay), and, on removing the combinable constituents, 7·45 c.c. were obtained from 660 c.c. of the gas. This is a greater proportion of argon than is present in air, being 1·14 per cent. No helium could be detected in the gas, nor were there any lines which could not be recognised as belonging to argon.

It has been thought worth while to place on record these experiments, although they show nothing remarkable. We have to express our indebtedness to Mr. Noel Heaton for help kindly rendered.

THE EXPANSION OF ARGON AND OF HELIUM AS COMPARED WITH THAT OF AIR AND HYDROGEN.*

By J. P. KUENEN, Ph.D.,
Professor of Physics in University College, Dundee, and
W. W. RANDALL, Ph.D.,
Lecturer in Johns Hopkins University, Baltimore, U.S.A.

ACCURATE comparisons of temperatures, as read with the aid of thermometers filled with different gases, have not often been made. The history of the subject may be said to have begun with the classical researches of Regnault ("Relations des Expériences," &c., 1847—62). Of recent work of this kind, that of Chappuis (*Archives de Genève* [3], vol. xx., pp. 5—36, 153—179, 248—262; also *Traités et Mémoires du Bureau International*, vol. vi.) was performed entirely at temperatures below 100°, the gases employed being hydrogen, nitrogen, and carbon dioxide. The experiments of Grunmach and Pernet (*Metronomische Beiträge*, No. 3) were also conducted at temperatures below 100°. Crafts (*Comptes Rendus*, vol. xcv., pp. 836—839), has compared the readings of a number of mercury thermometers with those obtained by Regnault and by himself with a hydrogen thermometer. Wiebe and Böttcher (*Zeitschrift fur Instrumentenkunde*, vol. x., pp. 16 and 233) have determined the boiling-points of a number of liquids in terms of the expansion of air.

In connexion with the work on argon and helium in progress at University College, it was suggested by Prof. Ramsay that a comparison should be made between the readings shown by thermometers containing respectively argon, helium, hydrogen, and air. The temperatures used were:—the melting-point of ice and the boiling-points of water, chlorbenzene, aniline, quinoline, and bromnaphthalene respectively. The gas to be experimented upon was contained in a bulb about 12 c.m. long and 2·2 c.m. wide, sealed at one end to a fine capillary tube about 12 c.m. long; this, in turn, was connected with a piece of thick-walled glass tubing, having an inside diameter of about 0·2 c.m. The wider tube was fitted with a stopcock, for convenience in filling the bulb, and at its lower end was connected with a stout rubber tube, which led to a movable mercury reservoir. Near the point at which the fine capillary tube was sealed to the wider tube, a mark was made on the latter: the mercury was always brought up to this mark in the experiments, and the difference of level in the tube and in the mercury reservoir was read off, with the aid of a telescope, from a glass scale graduated in millimetres, which stood directly behind the apparatus.

The bulb of the gas thermometer was heated in one of Ramsay and Young's vapour-jackets, the mark on the stem being just below the cork closing the bottom of the jacket: consequently a small portion of the stem was not heated to the temperature of the vapour in the jacket. The error thus introduced was taken into account. No part of the mercury column which compressed the gas in the bulb was heated more than a few degrees above the temperature of the room, screens being employed to cut off radiation: the temperature of the mercury was, however, always determined as accurately as circumstances would permit, and the readings reduced to 0°. In order to protect the thermometer bulb from the effects of radiation, the jacket was shielded by an outer cylinder of thick pasteboard, with an air space between.

Since the mercury was always brought to the same point on the stem of the thermometer bulb, the volume of the gas, except for the change produced by the expansion of the glass, was in all the experiments the same, while the pressure was, of course, different for each temperature employed. For convenience the bulb was filled, in the case of each gas, at from two-thirds to three-fourths atmospheric pressure: under these circumstances the bulb was never subjected to an internal pressure greater than about 1½ atmos.

Corrections.—All pressures were reduced to 0°. The coefficient of expansion of the glass of the bulb was carefully determined, and was found to be 0·00002804; its effect was allowed for. The effect of capillarity in depressing the mercury in the narrow tube was determined and taken into account. The volume of that part of the stem of the bulb which was not in the ice or vapour, as the case might be, was found to be 0·0003 of the whole, and was allowed for in the calculations. The change of volume in the bulb due to change of pressure was found to be negligible.

Gases.—The first gas experimented with was hydrogen. This was prepared from pure zinc, was washed with potassium permanganate solution and then with strong sulphuric acid, and was dried with phosphoric anhydride before it entered the previously exhausted bulb. The thermometer was successively filled and exhausted several times, in order to remove impurities, and was heated while vacuous to dislodge any gas clinging to the surface of the glass. Finally, the purified hydrogen was allowed to enter slowly until the required pressure was obtained.

Two sets of experiments were made with air. In the first set no effort was made to remove carbon dioxide, although the air was of course carefully dried. The readings were made by one of us alone, and, on account of

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* A Paper read before the Royal Society.

Kind of thermometer.	Corrected pressure 0°.	In steam at about 100°, the temperature being accurately calculated.	Coefficient of expansion at constant volume 0—100°.	Temperatures calculated.			
				Chlorbenzene.	Aniline.	Quinoline.	Bromnaphthalene.
1. Hydrogen	—	712·56	—	131·6	183·9	236·35	—
2. Air I.	—	737·74	—	131·8	183·6	[234·9]	281·65
3. Helium	567·02	775·18	0·003665	132·2	184·1	236·9	[278·3]
4. Argon I.	517·02	706·06	0·003668	132·15	184·1	—	—
5. Argon II...	529·54	—	—	—	—	237·8	281·5
6. Air II.	511·68	698·79	0·003663	—	—	237·1	—
Air (Wiebe)	—	—	0·003670	—	184·3	235·9	—
Temperature (R. and Y.)	—	—	—	132·1	184·4	237·4	280·4

the numerous details to be attended to which actually require the attention of two observers to be put beyond question, are probably not as accurate as the other series. The second series had to be brought to a close after the pressures corresponding to 0° and the boiling-points of water and quinoline had been determined. In this series care was taken to use air free from carbon dioxide.

The helium used was some of that prepared and purified by Professor Ramsay. Its density was 2·13, that of oxygen being taken as 16.

The argon employed was prepared from atmospheric air by the method of Professor Ramsay. A large gas-holder was filled with air which had been slowly drawn through a long combustion-tube filled with red-hot copper. This gas was dried, passed again over the hot copper, and then over red-hot magnesium shavings until absorption of nitrogen ceased. By these processes a gas was obtained consisting of about equal volumes of argon and nitrogen. Passage of this gas, backwards and forwards, through tubes containing respectively red-hot magnesium, red-hot copper oxide (to remove the hydrogen given off by the magnesium on heating), soda lime, and phosphoric anhydride, failed to remove the nitrogen completely. Finally, with the aid of a circulating apparatus (See Rayleigh and Ramsay, *Phil. Trans.*, 1895, A. p. 212), which ensured the passage of all the gas over the hot magnesium, a product was obtained whose density was found to be 19·99, oxygen being 16. The thermometer was filled with this gas.

After the pressures exerted by the argon when the bulb was surrounded by melting ice and by the vapours of water, chlorbenzene, and aniline, successively, had been determined, the thermometer was heated in the vapour of quinoline, when for some unknown reason, it cracked. A new bulb, of the same glass and as nearly as possible of the same size, was prepared, cleaned, and filled with argon, and a second series of readings made.

Finally, the argon was replaced by air, and the second series of readings for air, referred to above, begun. On account of the closing of the laboratory for the summer, this series was not carried as far as would have been desirable.

Temperatures.—The temperature of the jacket, when filled with steam from water boiling smoothly under atmospheric pressure, was taken from Kohlrausch's "Physical Measurements." The samples of the boiling liquids used were re-distilled, and were found to pass over without a rise in temperature of more than a tenth of a degree, in three cases; of a fifth of a degree in the fourth case.

The results of our observations are laid down in the table. In three cases (3, 4, and 6) the reading was taken at 0°, as well as at the boiling-point of water; this enabled us to calculate the coefficient of expansion between these two points. The result is shown in the fourth column. The higher temperatures determined with these thermometers have been derived from the observed pressures by using the coefficients thus measured. As the barometric pressures differed, more or less, from the normal value, the boiling-points had to be reduced to normal pressure, for which operation we made use of the differences in Ramsay and Young's well-known tables (*Chem. Soc. Journ.*, vol. xlvii., p. 640; vol. lv., p. 483). In calculating the temperatures of air thermometer I., where the reading at 0° had been omitted, and of argon thermometer II., where we did not take the reading in steam, we used the coefficients found with air thermometer II. and argon thermometer I., respectively, in the first case basing our calculations on the reading in steam. With the hydrogen thermometer, where the reading at 0° had not been taken, we accepted 0·003663 as the coefficient of that gas, and based our calculations of the temperatures again on the reading in steam.

Since the readings of the mercury surfaces, with the gas thermometer as well as the barometer, were taken on a millimetre scale, an occasional mistake in the final pressure of 0·1 or 0·2 m.m. is by no means excluded. Uncertainties of that amount do not, however, account for the differences between the results obtained with the different thermometers. The readings of air thermometer I. are, perhaps, somewhat less to be relied upon than the others, because they had to be observed, as was stated above, by one of us in the absence of the other. The boiling-point of bromnaphthalene, as determined with the helium thermometer, is also very uncertain, because the position of the mercury was not at all stable, probably on account of the difficulty of obtaining rapid and smooth boiling of the liquid. Yet, even if these values are not taken into account, the differences are very remarkable, especially with quinoline, and the agreement with Wiebe's result is also not quite satisfactory. Part of these differences may be due to impurity in the liquids used in the jacket. Pains were taken at the beginning of our experiments to have them quite pure, but as the values show, apparently, a tendency to rise, it may be that continuous boiling produced slight decomposition. In the case of bromnaphthalene this is more than possible. If more time had been at our disposal we should have tested the purity of our substances during the operations. As it is now, it would be unwise to draw conclusions from our figures about the exact behaviour of any of the gases used at high temperatures. The coefficients of expansion between 0° and 100° found for argon and helium agree very well with the values usually found for gases, and there is no indication of anything extraordinary happening to these gases at high temperatures. When argon thermometer I. was heated in the vapour of quinoline, a remarkable expansion of the gas was observed, continuing for two hours until a maximum value was reached; this gave an apparent temperature of 243·5° for the boiling-point of quinoline. On cooling the thermometer, however, it was found to be cracked, and some drops of quinoline were noticed inside the bulb. The measurements made in this case were therefore rejected, and a new series was begun with argon thermometer II., which gave a value about normal. How the quinoline could have found its way into the bulb while an interior pressure of about 970 m.m. existed within it, without the argon escaping rapidly at the same time, is not quite clear. It may be the vapour passed through the crack when the temperature was rather low, and that the opening was closed by the later expansion of the glass.

For completeness sake, we give in the table the boiling-points of the same substances determined with a mercury thermometer, as calculated from Ramsay and Young's tables. But the irregularities of the thermometers prevent our giving any definite numbers for the reduction of those tables to accord with any of the gas thermometer scales. A direct comparison, such as was executed by Wiebe and Böttcher, with a mercury thermometer of known constitution, like the Jena glass thermometer, would have been desirable. Differences of boiling-point resulting from impurities would have affected both thermometers in the same way, and would have enabled us to ascertain how much of the differences found resulted from that source of error. But here also want of time prevented our extending our programme beyond the limits fixed beforehand.

Notwithstanding the incompleteness and want of perfection of our work, we do not hesitate to publish our results; the difficulties to be overcome in experiments of this kind are serious, and we did not make it our object to obtain results of remarkable accuracy. The real motive of the work was to discover whether argon and helium show extraordinary behaviour at high tempertures, or not,—and our results apparently establish the fact that they do not. Their behaviour, so far as expansion is concerned and within the limits of temperature which we used, is apparently the same as that of so-called perfect gases or mixtures of them.

Finally, it is a great pleasure to record our hearty appreciation of the kindly assistance of Professor Ramsay, at whose suggestion, and under whose supervision, these experiments have been conducted.

HELIUM AND ARGON: THEIR PLACES AMONG THE ELEMENTS.

By R. M. DEELEY.

The discovery by Lord Rayleigh and Professor Ramsay of two new elements having small atomic weights has undoubtedly had the effect of greatly shaking the confidence of chemists in the periodic classification of the elements. Indeed, a disposition is often shown to place the Periodic Law altogether in the background and put undue faith in physical evidence, which is admitted to be inconclusive.

Although we cannot hope, in the present state of our knowledge, to pronounce a definite opinion in favour of any one of the hypotheses advanced, it may not be out of place to review the facts from the standpoint of the Periodic Law.

In Table I. all the best known elements are placed in the order of their atomic weights. To bring elements having similar properties into the same vertical lines, it has been necessary to leave many blanks. For instance, on the first line sixteen such blanks have been left, hydrogen and helium falling on the last two spaces.

"Every element," according to Mendeleeff ("The Principles of Chemistry," vol. ii., p. 23), "occupies a position determined by the group and series in which it occurs. For instance, Se occurs in the same group as $S=32$ and $Te=125$, and in the same series as $As=75$ and $Br=80$; hence the atomic weight of selenium should be $\frac{1}{4}(32+125+75+80)=78$, as it is in reality." "*In this manner it is possible to foretell the properties of still unknown elements.*" As Mendeleeff does not arrange the elements as they are placed in the first three lines of Table I., his argument does not apply to them. Indeed, he expressly omits elements having atomic weights smaller than aluminium from his calculations, and calls them *typical elements*. We must not, therefore, suppose that because argon and helium do not fall satisfactorily into his system that his arrangement is altogether wrong. These elements should fall among his *typical elements*, the classification of which is admittedly imperfect. Even as placed in Table I., grave fault may be found with the arrangement. Hydrogen, although it may be conveniently classed with F, Cl, Br, and I, is a metallic element. Beryllium and magnesium may also, with some reason, be placed in the column with zinc and cadmium, and lithium and sodium with copper and silver. There is consequently grave doubt whether the blank spaces in the first three lines are really blanks for elements not yet discovered. It would be rash to suggest that there are sixteen elements having smaller atomic weights than hydrogen, for instance.

I have elsewhere* shown that there are good reasons for supposing that no such blanks really exist, the *typical* elements occupying the whole of the first line above that commencing with potassium, as in Table II.

In my paper published in 1893 I showed that there was a blank for *one* element between H and Li. To this element I gave an atomic weight of about 2·5 (p. 861). If the element be monatomic, this is about half as large as it should be; but if diatomic, it is not far wrong. Professors Runge and Paschen have suggested that helium is really a mixture of two gases, but the spectroscopic evidence cannot be regarded as very satisfactory.

The difficulty of placing argon in position in the Periodic Table is, however, much greater. Is it monatomic or diatomic? If monatomic, as is generally supposed, its atomic weight would place it between potassium and calcium—a position which would not agree with our present reading of the Periodic Law (*Nature*, Sept. 26, 1895, p. 537). Its refraction equivalent also indicates 20 rather than 40, and places it between fluorine and sodium, as shown on Table II. The only argument supporting the monatomic view is that derived from a consideration of the ratio of specific heats. This is often regarded as conclusive. Such, however, is not the case. Mr. J. W.

Table I.

—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	H	He
Li	Be	—	—	—	—	—	—	—	—	—	—	B	C	N	O	F	A
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	Di	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—	—
—	—	—	Th	—	U	—	—	—	—	—	—	—	—	—	—	—	—

Table II.

H	He	Li	Be	B	C	N	O	F	A	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	Di	?	?	?	?	?	?	?	?	?	?	?	?	(?)
?	?	Yb	?	Ta	W	?	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	?	?	(?)
?	?	?	Th	?	U	?	?	?	?	?	?	?	?	?	?	?	(?)

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* "A New Diagram and Periodic Table of the Elements" (*Trans. Chem. Soc.*, 1893); "The Oxides of the Elements and the Periodic Law" (*Trans. Chem. Soc.*, 1894); "The Refraction Equivalents of the Elements and the Periodic Law" (*Trans. Chem. Soc.*, 1894).

Capstick (*Science Progress*, 1895, vol. iii., p. 281) says:—"After all, in our present state of ignorance regarding the status of the atom in the molecule, the argument drawn from the ratio of the specific heats is little more than an argument from analogy. The question at issue seems to be just the sort of case where the argument may break down, for argon differs in such a remarkable way from all other known substances that it would be unsafe to deny the impossibility of further eccentricities in the dynamics of its molecule."

Under such circumstances would it not be well to follow the indications of the Periodic Law and refraction equivalents rather than a doubtful theory concerning the dynamics of the molecule?

ON THE TECHNICAL ANALYSIS OF CYANIDE WORKING SOLUTIONS.*

By W. BETTEL.

(Concluded from p. 287).

4. *Ferrocyanides and Sulphocyanides.*—In absence of organic matter, I have found that an acidified solution of a simple cyanide, such as KCy, or a double cyanide (as K_2ZnCy_4), *i.e.*, solution of HCy, is not affected by dilute permanganate. On the other hand, acidified solutions of ferrocyanides and sulphocyanides, are rapidly oxidised—the one to ferrocyanide, the other to $H_2SO_4 + HCy$.

$$2K_4FeCy_6 + O + H_2SO_4 = K_6Fe_2Cy_{12} + K_2SO_4 + H_2O.$$
$$2KCNS + 2H_2O + 3O_2 = 2KHSO_4 + 2HCy.$$

If now, the ferrocyanogen be removed as Prussian blue, by ferric chloride in an acid solution, the filtrate will contain ferric sulphocyanide and hydric sulphocyanide, both of which are oxidised by permanganate as if iron were not present; by deducting the smaller from the larger result, we get permanganate consumed in oxidising ferrocyanide, the remainder equal permanganate consumed in oxidising sulphocyanide.

The method of analysis is as follows (in presence of zinc):—A burette is filled with the cyanide solution for analysis, and run into 10 or 20 c.c. N/100 $K_2Mn_2O_8$ strongly acidified with H_2SO_4 until colour is just discharged. Result noted (*a*).

A solution of ferric sulphate or chloride is acidified with H_2SO_4 and 50 c.c. of the cyanide solution poured in. After shaking for about half a minute, the Prussian blue is separated from the liquid by filtration and the precipitate and filter paper washed. The filtrate is next titrated with N/100 $K_2Mn_2O_8$ (*b*).

Let c = c.c. permanganate required to oxidise ferrocyanide.
Then $a - b = c$.

(*c*) 1 c.c. N/100 $K_2Mn_2O_8 = 0{\cdot}003684$ grm. K_4FeCy_6.
(*b*) 1 c.c. N/100 $K_2Mn_2O_8 = 0{\cdot}0001618$ grm. KCNS.

5. *Oxidisable Organic Matter in Solution.*—In treating spruit tailings, or material containing decaying vegetable matter, I offer the following method for testing coloured solutions:—

(*a*) Prepare a solution of a sulphocyanide, so that 1 c.c. sulphocyanide = 1 c.c. N/100 $K_2Mn_2O_8$.
(*b*) To 50 c.c. solution add sulphuric acid in excess, and then a large excess of permanganate, N/100. Keep at 60—70° C. for an hour. Then cool and titrate back with the KCNS solution.

Result O consumed in oxidising organic matter.
„ O „ „ K_4FeCy_6.
„ O „ „ KCNS.

After estimating KCNS and K_4FeCy_6, a simple calculation gives the oxygen to oxidise organic matter. This result multiplied by 9 will give approximately the amount of organic matter present.

In order to clarify such organically charged solutions, I shake them up with powdered quicklime, and filter; the solution is then of a faint straw colour, and is in a proper condition for analysis. In such clarified solution the oxidisable organic matter is no longer present, and the ferro- and sulphocyanogen estimations are readily performed.

6. *Alkalinity.*—Potassic cyanide acts as caustic alkali, when neutralised by an acid; the end-reaction, however, is influenced to some extent by the hydrocyanic acid present, and is therefore not sharp. We can, however, estimate—

By	N/10 acid 100 % KCy N/10 acid 7·9 % of K_2ZnCy_4	With phenolphthalein as indicator.
	N/10 acid 100 % of zinc in K_2ZnCy_4 N/10 acid 100 % of Zn+K in ZnK_2O_2	With methyl-orange as indicator.
	N/10 acid the K_2O in ZnK_2O_2	With phenolphthalein as indicator.

It will be necessary to point out the decompositions which result from adding alkali, or a carbonate of an alkali, to a working solution containing zinc.

$$K_2ZnCy_4 + 4KHO = ZnK_2O_2 + 4KCy.$$
$$K_2ZnCy_4 + 4Na_2CO_3 + 2H_2O = \\ = 2KCy + 2NaCy + ZnNa_2O_2 + 4NaHCO_3.$$

Bicarbonates have no action upon potassic or sodic zinc cyanide.

Potassic or sodic zinc oxide (in solution as hydrate) acts as an alkali towards phenolphthalein and methyl-orange.

$$ZnK_2O_2 + 4HCl = 2KCl + ZnCl_2 + 2H_2O.$$

Calcic and magnesic hydrates decompose the double salt of K_2ZnCy_4 to some extent, but not completely, so that it is possible to find in one and the same solution a considerable proportion of alkalinity towards phenolphthalein, due to calcic hydrate in presence of K_2ZnCy_4.

The total alkalinity as determined by N/10 acid with methyl-orange as indicator gives, in addition to those before mentioned, the bicarbonates. If to a solution containing sodic bicarbonate and potassic zinc cyanide be added lime or lime and magnesia, the percentage of cyanide will increase, the zinc remaining in solution as zinc sodic oxide.

7. *Ferricyanide Estimation.*—This is effected by allowing sodium amalgam to act for fifteen minutes on the solution in a narrow cylinder, then estimating the ferrocyanide formed by permanganate in an acid solution. Deduct from the results obtained the ferrocyanide and sulphocyanide previously found, 1 c.c. N/100 permanganate = 0·003293 grm. $K_6Fe_2Cy_{12}$.

8. *Sulphides.*—It rarely happens that sulphides are present in a cyanide solution; if present, however, shake up with precipitated carbonate of lead, filter, and titrate with permanganate N/100. The loss over the previous estimation (of K_4FeCy_6KCNS, &c.) is due to elimination of sulphides.

1 c.c. N/100 $K_2Mn_2O_8 = 0{\cdot}00017$ grm. H_2S
or—
1 „ „ „ $= 0{\cdot}00055$ „ K_2S.

The hydrogen alone being oxidised by dilute permanganate in acid solution where the permanganate is not first of all in excess.

9. *Ammonia.*—If sufficient nitrate of silver be added to a solution (say 10 c.c.) to wholly precipitate the cyanogen compounds and a drop or two of normal hydrochloric be added in addition, the whole made up to 100 c.c., and

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* A Paper read before the Chemical and Metallurgical Society, Johannesburg, S.A.R., August, 1895.

shaken, then filtered, and 10 c.c. filtrate distilled with 150 c.c. water from a tubulated flask, and the steam condensed in a Liebig's condenser (glass), the ammonia coming over may be readily estimated by colour test with Nessler solution and comparison with distilled water free from ammonia and standard ammonic chloride solution containing 0·01 m.grm. per litre, treated with Nessler solution.

Then 10 c.c. taken diluted to 100 c.c.
10 „ from 100 c.c. = 1 c.c. original
= 1000 m.grms., then every 1 c.c. standard solution of ammonic chloride taken = 0·001 per cent NH_3.

Urea, Oxamide, and Formates.—I am still investigating a method for the determination of these substances.

Although these reactions and processes take some time in describing, the whole of the operations can be performed within one hour, and once the operator has a practical knowledge of the process, the results, provided he is sure of the accuracy of the titre of his stock solutions, are most accurate. Most valuable information can in this way be obtained. I give a few instances of the analysis of working solutions :—

1. Solution (originally KCy) in contact with clean pyrites from Robinson concentrates for twenty-eight months with a limited supply of air :—

	Per cent.
Potassic ferrocyanide	0·77
Potassic sulphocyanide	0·14
Potassic cyanide	0·005
Potassic carbonate	0·33
Potassic formate, present but not estimated	—
Ammonia	0·21
Sulphides, absent	—
Sulphates, considerable, not estimated	—

2. Solution from treating dry crushed Robinson G. M. Company's ore without addition of neutralising agents after passing through zinc box :—

	Per cent.
Potassic cyanide	0·085
Potassic-zinc cyanide	0·25
Potassic-zinc hydrate	0·15
Potassic ferrocyanide	0·c74
Potassic sulphocyanide	0·004
Potassic bicarbonate	0·566
Ammonia	0·808

3. As above, but with use of lime, not passed through zinc box :—

	Per cent.
Potassic cyanide, original 0·3 per cent	0·24
Potassic ferrocyanide	trace
Potassic ferricyanide	0·033
Potassic sulphocyanide	0·008
Ammonia	0·003
Calcic hydrate	0·067

4. As in No. 2, but with lime in small quantity, after passing zinc box :—

	Per cent.
Potassic cyanide, original 0·45 per cent	0·23
Hydrocyanic acid	0·04
Potassic-zinc cyanide	0·154
Potassic ferrocyanide	0·059
Potassic sulphocyanide	0·004
Potassic sulphate	nil
Potassic bicarbonate	0·547
Ammonia	0·006

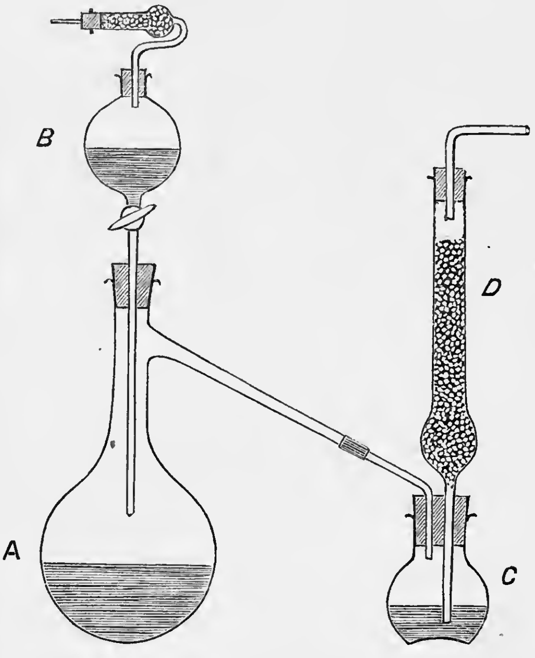
It will be unnecessary to quote more analyses. A better way will be for chemists and cyanide works managers to adopt the process and compare results from analysis of their different solutions.

APPARATUS FOR THE ESTIMATION OF SULPHUR IN IRON.

By E. J. READ, B.A.

In the estimation of sulphur in iron the following apparatus is very efficient and convenient, and could probably be used for other purposes:—

The sample is placed in A, the acid in B. The side-tube of A is connected with the wash-bottle C, to which a calcium chloride tube D, filled with glass beads, is attached. The tube of D dips a regulated distance below the surface of the absorbing liquid, so that this is forced up among the beads by the passage of the evolved gas, and a most efficient absorption is obtained with the use of only a small quantity of absorbent. If the inlet tube of C dips below the surface of the liquid, it must be raised before disconnecting the apparatus, to prevent loss of liquid. The operation is preferably conducted under reduced pressure, and a current of pure air may be run through the apparatus at the conclusion to sweep out the remaining traces of gas from A.



BOILING-POINT AND THE GENESIS OF THE ELEMENTS.

By C. T. BLANSHARD, M.A.

In a late number of the Chemical News (vol. lxxi., p. 285) I drew a parallel between the elements and certain organic compounds, establishing a connection between melting-point and periodic groups on the one hand, and melting-point and structure on the other. In the following article I hope to show that the physical property of volatility is equally valuable as a clue to the relationship of the elements to one another.

Data as regards the boiling-points of elements are still very defective; but, if we examine into the elements group by group, we shall soon see that definite laws of volatility hold. Thus we have in—

Group.	Element.	B. p.	Diff.	Observer.
I.	Na	742°		Perman.
			75°	
	K	667°		Perman.
II.*a.*	Zn	940°		Violle.
			170°	
	Cd	770°		Carnelley.
			213°	
	Hg	357°		Regnault.
	Mean diff. ..		191°	

In Groups II., III., &c., there are not data enough.

Group.	Element.	B. p.	Diff.	Observer.
V.	N	−194°		Wroblewski; Olszewski.
			483°	
	P	+289°		Dalton; Pelletier.
			71°	
	As	360°		Engel.
			1080°	
	Sb	1440°		Carnelley & Williams.
			340°	
	Bi	1700°		Mensching and V. Meyer; Biltz and V. Meyer.
	Mean ..		496°	
VI.	O	−181°		Olszewski; Wroblewski.
			629°	
	S	+448°		Regnault.
			232°	
	Se	680°		Carnelley.
	Mean ..		430°	
	Te	?		
VII.	F	?		
	Cl	−34°		Regnault.
			97°	
	Br	+63°		Pierre; Stas; van der Plaats.
			121°	
	I	184°		Ramsay and Young.
	Mean ..		109°	

The values are from Landolt and Börnstein, "Physikalische-chemische Tabellen," 1894; except that for iodine, which is from the last edition of "Watts' Dict. Chem."

From the above tables we may fairly induce the following laws for the elements regarding boiling-point:—

1. In the metallic groups (*i. e.*, I. to IV. inclusive) the volatility varies directly as the atomic weight, whilst the differences between the successive boiling-points are more or less constant.
2. In the non-metallic groups (*i. e.* V. to VII. inclusive) the volatility varies inversely as the atomic weight, whilst the differences between successive boiling-points alternate to a marked degree.
3. The mean differences gradually increase up to Group V., or group of the highest general atomicity, and then again gradually diminish.

Let us now, with these facts in view, see what maintains in various groups of organic compounds, taking some of less, others of greater complexity.

Karl Windisch, in his "Beziehungen zwischen den Siedepunkt u. der Zusammensetzung Chem. Verbindungen," Berlin, 1889, quotes the researches of the following: (the abbreviations are those used in "Watts' Dictionary")—Kopp (A. 41, 79; A. Supp. 5, 321; A. 96, 1; 50, 79; Schorlemmer (A. 161, 281); Linnemann (A. 162, 41); Hantsch (A. 115, 36); Schmidt (B. 5, 597; 6, 498); Michaelis (B. 8, 499); Goldstein (J. R.); besides Naumann, Schreiner, Henry, Denzel, Sabæneyeff, Kahlbaum, Staedel, and Mills. He finds that all these researches point to the comparative constancy of the *differences* between the boiling-points in various organic series. Each organic series, he shows, has its own constant difference for every increment of CH_2. Thus for (1) 25 alcohols he finds the average difference to be 19·5°; (2) 71 fatty acids, average diff. = 21·5°; (3) mercaptans, average diff. = 29°.

Windisch remarks on these figures that "the differences in nearly all cases are very near the average differences given." But the facts really point to a different and most interesting conclusion.

I will take certain organic series which are tolerably complete as to boiling-points, besides being well authenticated. The temperatures are from Victor Meyer and Paul Jacobson, "Lehrbuch der organ. Chemie" (Veit and Co., Leipzig, 1893). I have added the differences, selecting only the *normal* compounds to base them upon.

1. *Normal Paraffins.*

Formula.	B.-p. °	Diff. °
C_4H_{10}	1	
		36
C_5H_{12}	37	
		32
C_6H_{14}	69	
		39
C_7H_{16}	98	
		27
C_8H_{18}	125	
		25
C_9H_{20}	150	
		23
$C_{10}H_{22}$	173	
		22
$C_{11}H_{24}$	195	
		19
$C_{12}H_{26}$	214	
		20
$C_{13}H_{28}$	234	
		18
$C_{14}H_{30}$	252	
		18
$C_{15}H_{32}$	270	
		17
$C_{16}H_{34}$	287	
		16
$C_{17}H_{36}$	303	
		14
$C_{18}H_{38}$	317	
	Average ..	23·3

2. *Normal Primary Alcohols.*

Formula.	B.-p. °	Diff. °
$CH_3.OH$	66	
		12
$C_2H_5.OH$..	78	
		19
$C_3H_7.OH$..	97	
		20
$C_4H_9.OH$..	117	
		21
$C_5H_{11}.OH$	138	
		19
$C_6H_{13}.OH$	157	
		19
$C_7H_{15}.OH$	176	
		19
$C_8H_{17}.OH$	195	
		18
$C_9H_{19}.OH$	213	
		18
$C_{10}H_{21}.OH$	231	
	Average ..	19·5

3. *Normal Primary Aldehyds.*

Formula.	B.-p.	Diff.
	°	°
$CH_3.COH$	21	
		28
$C_2H_5.COH$	49	
		24
$C_3H_7.COH$	73	
		29
$C_4H_9.COH$	102	
		26
$C_5H_{11}.COH$	128	
		27
$C_6H_{13}.COH$	155	
		16? (25?)
$C_7H_{15}.COH$	171?	
	Average ..	26·5

4. *Normal Fatty Acids.*

Formula.	B.-p.	Diff.
	°	°
$H.CO_2H$	101	
		17
$CH_3.CO_2H$	118	
		13
$C_2H_5.CO_2H$	141	
		21
$C_3H_7.CO_2H$	162	
		23 (exceptional).
$C_4H_9.CO_2H$	185	
		20
$C_5H_{11}.CO_2H$	205	
		18
$C_6H_{13}.CO_2H$	223	
		13
$C_7H_{15}.CO_2H$	236	
	Average ..	18

5. *Primary Ethyl Esters.*

Formula.	B.-p.	Diff.
	°	°
$HCO_2.C_2H_5$	55	
		22·5
$CH_3CO_2.C_2H_5$	77·5	
		21·5
$C_2H_5CO_2.C_2H_5$	99	
		22
$C_3H_7CO_2.C_2H_5$	121	
		24 (exceptional).
$C_4H_9CO_2.C_2H_5$	145	
		22
$C_5H_{11}CO_2.C_2H_5$	167	
		20
$C_6H_{13}CO_2.C_2H_5$	187	
		19
$C_7H_{15}CO_2C_2H_5$	206	
		21·5
$C_8H_{17}CO_2.C_2H_3$	227·5	
	Average ..	21·5

6- *Normal Primary Mercaptans.*

Formula.	B.-p.	Diff.
	°	°
$CH_3.SH$	6	
		30
$C_2H_5.SH$..	36	
		31
$C_3H_7.SH$..	67	
		30
$C_4H_9.SH$.. ,, ...	97	
	Average ..	30·3

7. *Normal Primary Ketones.*

Formula.	B.-p.	Diff.
	°	°
$(CH_3)_2.CO$	56	
		47
$(C_2H_5)_2.CO$	103	
		41
$(C_3H_7)_2.CO$	144	
		37
$(C_4H_9)_2.CO$	181	
		46
$(C_6H_{11})_2.CO$	227	
		37
$(C_6H_{13})_2.CO$	264	
	Average ..	42

In the above series we notice:—

1. Following Windisch's method, the average differences in boiling-point are as follows:—

		Mean diff.
1.	Normal primary acids..	18
2.	,, ,, alcohols	19·5
3.	,, ,, ethyl esters ..	21·5
4.	,, ,, paraffins	23·3
5.	,, ,, aldehyds	26·5
6.	,, ,, mercaptans ..	30·3
7.	,, ,, ketones	42

2. The more complex the members of any series, *i.e.*, the more they deviate from the simple structure of the water type, the greater the mean difference.

3. In all the above series the differences alternate with more or less regularity; but in the series of least differences the alternation is least, the differences approaching a constant; whilst the series of greatest differences show the greatest alternations.

In all organic series the volatility varies inversely as the atomic weight.

With the above-mentioned exception, the laws relating to the difference of boiling-point of organic compounds, and the alterations of the same, show a close connection with Laws 1 and 2 applying to the elements.

A comparison of the data so far brought to bear on the subject and the laws induced from these data, leads us to the conclusion that, of the elements, Groups I. to IV. —of general valency one to four—are less highly evolved than Groups V. to VII.—of increasing valency with regard to oxygen, and of decreasing valency with regard to hydrogen.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 286).

On the Methods used to ascertain whether Solid Bodies were Present in or Absent from Chlorate, Perchlorate, and Chloride of Potassium.

To verify the absence or presence of iron, manganese, copper, aluminium, and silicon, in chlorate, perchlorate, and chloride of potassium, I argued from the following facts:—

Chlorate and perchlorate, when dissociated by the action of heat in a pure polished platinum dish, are clearly transformed into chloride and oxygen without liberating a trace of chlorine. The evolution of chlorine, detected by all chemists during the decomposition of these salts by the action of heat, is due to the presence of foreign bodies in the compounds submitted to dissociation, and especially to the presence of iron, manganese, copper, aluminium, or silicon.*

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* In a memorandum added to the chapter on the "Preparation of Pure Chlorate, Perchlorate, and Chloride of Potassium," I describe

Fused chloride of potassium is *colourless*, or more or less coloured *red*, *pink*, or *green*, according as it is free from or contains iron, manganese, or copper.

When heated beyond its fusing-point, colourless chloride of potassium — except it contains aluminium, silicon, or calcium—volatilises without leaving a trace of residue.

If the quantity of aluminium and silicon, in the form of aluminous silicate or silica, exceeds about 1-5000th of the whole in weight, the chloride of potassium when melted immediately shows brilliant specks floating on the liquid, caused by alumina or silica, or silicate of aluminium. In the other case, one only sees the brilliant specks appear on volatilising chloride by heat, when the proportion of alumina or silica, or silicate of aluminium, is brought to about 1-5000th of the weight of chlorine.

If the silicon is in the chloride in the form of silicate of potassium or sodium, as is generally the case, the chloride when melted is a homogeneous liquid, even though the proportion of silicate be raised to a considerable percentage of the weight.

Dull platinum, and even this metal when polished, are wetted by melted chloride of potassium. Thus, when volatilising a chloride containing either silicate of potassium or silicate of sodium, you may see that—in proportion as it evaporates—the chloride leaves *concentric circles* of solid silicate, which keep increasing in thickness.

The appearance of these concentric circles is so constant that one can rely on them, as I have done during the preparation of pure chlorate, to judge of the degree of purification as regards the elimination of silica combined with potassium and sodium.

When applying this method of research to the chloride obtained from so-called pure chlorate of potassium from chemical manufactories, I have relied on the same rings to show me the large quantity of solid matters left on evaporation.

To verify the above facts, I have volatilised the chloride of potassium in a concave lid of a large pure platinum retort with wide flat edges, holding 10 or 12 grms. of melted chlorate. This lid rested by its border on a ring made of very thick platinum wire, supported by *three* blocks of fire-clay. These blocks were arranged so as to form a passage shut on one side, opened on the other, intended to hold a coal-gas blowpipe worked by bellows, and to serve for carrying off the products of combustion. The coal-gas and air blowpipe was arranged so as to give the highest possible temperature at the *centre* of the platinum lid, whilst raising its flat rim to a red heat so as to unite it to the ring which supported it. The flat rim completely covering the ring, the products of combustion could not escape around the dish, and were obliged to pass away by the upcast channel.

When working the apparatus in a closed room, the air of which has been purified by remaining still for at least twelve hours, one can go on with the volatilisation of the chloride without it being necessary to place, at a certain distance above the lid, a sheet of platinum to prevent the dust, known to be always in air in motion, from falling into the chloride. I will add that I have proceeded in this manner during the numerous *qualitative analyses* I have made, as well for ascertaining the degree of purity of the chloride got by dissociating so called pure chlorate supplied by dealers in chemicals, as to judge of the state of progress in purifying the chlorides got from the decomposition of those chlorates of potassium.

When I have been making a *quantitative analysis* I have taken care to suspend, by a platinum wire, a large sheet of this metal in a very inclined position, and near enough to the surface of the dish to diminish the current which exists whatever one may do, and to prevent the projection into it of foreign bodies by draughts.

By regulating the blowpipe, both for the amount of gas burnt and for its position, one can volatilise in free air about 10 grms. of chloride of potassium in *from eighteen to twenty minutes*, by the method I have just described. On the other hand, it requires at least *thirty minutes* when placing a large sheet of platinum at a great inclination above and near the surface of the evaporating dish. In this case a certain part of the volatilised chloride is deposited in a crystalline, transparent, and colourless state, in the centre of the sheet, surrounded by a snowy border. One could use this deposit for obtaining chloride free from all solid bodies, if it were not easier and more certain to obtain it free from all solid bodies, and from the sodium of the air, by the method described above, which I have twice done on a large scale, as I shall describe further on.

I have compared the result arrived at by this quick method with that very much longer one I described in my "New Researches on the Laws of Chemical Proportions," and which consists in performing the volatilisation in a platinum boat, placed in a porcelain tube covered inside with platinum, and raised to white heat, and causing a current of dry nitrogen to pass through it.

When applying purified nitre with the greatest care to part of the chloride in which I had found, by the latter method, 0·00056 grm. of solid residue, I found by the new method 0·00060 grm. per 10 grms. experimented on. Both methods are evidently of equal value.

To finish this description I ought to add that experience has shown me that one cannot rely on the weight of the platinum vessel keeping constant when heated *in the coal-gas and air blowpipe*. I have often found the weight slightly increased, but more often decidedly decreased. When one wishes to get as accurate results as possible, one must weigh the platinum vessel on which one has evaporated the chloride, and weigh it again after having allowed hydrofluoric acid mixed with its own volume of water to remain *in the cavity in the cold*, and then hydrochloric acid diluted to 1-20th; and lastly, after having washed it enough with pure water. Under these conditions pure platinum does not change in weight.

By taking the difference between the first and second weight of the platinum vessel when heated to white heat and then cooled under a bell-jar in air of the same dryness, as the weight of the residue, one is bound to get a result as accurate as a research of this nature permits of.

To look for *calcium* in the chlorate and chloride of potassium I employed spectrum analysis; but the quantity of this metal being seldom enough to be seen in the compounds put into the flame, I have, after having transformed the chlorate into chloride, volatilised it down to a few hundredths of its volume. I then put the residue into a Bunsen flame or into an oxyhydrogen blowpipe flame, to look for the characteristic lines of the calcium spectrum. By doing this, one is easily convinced of the extreme difficulty of obtaining chlorate or chloride of potassium absolutely free from calcium.

On the Preparation of Chlorate of Potassium.

After having ascertained that, by means of a very dilute solution of sulphydrate or hydroxide of potassium, one can transform the silicon and sodium in chlorate of potassium to a *silicate*, I have, on two different occasions, proceeded with the purification of commercial chlorate, which I had submitted to a preliminary analysis, working the first time on *three kilogrms.* and the second time on *two kilogrms.* of this salt from different sources. The chlorate to be purified contained iron, manganese, copper, a great deal of sodium, silica, aluminium, magnesium, calcium, chlorides and sulphates, as well as organic dust. I effected the purification in the following manner:—

To a sufficient quantity of water, kept at about 100° in two large porcelain dishes, was added, to saturation, the powdered chlorate, and the solution was filtered to get rid of the dust in suspension. The filtered liquid, having been again brought to about 100°, received an excess of a

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the method I used to ascertain whether chlorine were present in or absent from oxygen produced by the decomposition of absolutely pure chlorate an perchlorate of potassium by heat.

dilute solution of sulphydrate of potassium,* and was filtered immediately. On suddenly cooling it the solution precipitated a salt in small *pink* flakes. The mother-liquor, which was coloured, was completely separated. The salt was put into a large shallow funnel, fitted with a clean linen plug, and a smooth ground-glass cover with a hole in it. The funnel was fitted on to a large flask with two tubes communicating with a water-pump. After straining the salt in pure air it was sprinkled with iced water containing about one per thousand of sulphydrate of potassium, keeping the pump at work until the chlorate was rendered completely colourless. The sulphydrate solution was followed by pure iced water, to remove the alkali and foreign salts as much as possible.

The colourless saline flakes were finely powdered in a Wedgewood mortar, and the powder was replaced in the large funnel and washed afresh with pure iced water.

The chlorate, when treated thus, had a very decided sodic reaction. It was saturated with water at 100°. The solution, not being clear, was filtered, and to the liquid—heated to re-dissolve all the chlorate which had been crystallised by cooling—was added a solution of sulphydrate in sufficient quantity to give it an *alkaline reaction.* The liquid was neither cloudy nor coloured, and the chlorate which was precipitated on suddenly cooling it was in fine colourless flakes.

The salt was strained and washed with a wash-bottle, first with iced water containing one per thousand of sulphydrate of potassium, and then with pure iced water. The sodium lines were distinctly visible on analysis, but by no means so clearly as in the case of the chlorate from which the salt was made.

When dissolved in water it did not cloud a solution of chloride of barium, but it did very sensibly nitrate of silver.

I repeated a third time, in porcelain, the treatment I have just described, and, although I was obliged to work in the soda-contaminated air of the laboratory, the chlorate showed the sodium characteristics in a Bunsen burner so faintly that it was necessary to resort to spectrum analysis before being able to detect with certainty the presence of sodium in it.

The solution of salt no longer clouded nitrate of silver, but the chlorate, when decomposed by heat, evolved a sensible amount of chlorine, and the chloride formed from it—when volatilised by the method mentioned above—left a small residue in which I detected the presence of silica, potassium, sodium, aluminium, and calcium.

Having learnt, as I have described above, by preliminary trials, that, by continuing the treatment in porcelain or glass tubes, one introduces as much silica and sodium into the chlorate as the use of sulphydrate of potassium enables one to eliminate from it, I continued the operations entirely in platinum, and, as far as possible, in enclosed and purified air. For this purpose I dissolved it in boiling water in a large platinum retort with a lid, *the neck of which contained a large cotton plug washed with a mixture of ether and alcohol, dried, and then soaked in a saturated solution of chlorate of potassium.*

As soon as the water was saturated the liquid was made alkaline by sulphydrate of potassium, and immediately cooled by plunging the retort into running cold water, and finally into snow. By inclining the retort to one side the mother-liquor was drained off by the opening in the neck of the dome, from which the cotton plug soaked in the chlorate solution was removed. By plunging a hard rubber tube, treated successively with a dilute boiling solution of pure potassium with dilute acetic acid, and then with pure water, into the saline mass, the remaining mother-liquor was drawn by suction; this was replaced several times with small quantities of iced water containing hydrate of potassium. and then with pure iced water, until the liquor was quite neutral to litmus-paper.

After this *fourth* treatment, the salt, when introduced into a Bunsen flame, gave it a *pale blue* colour. At the time of making this experiment the air of the large room in which I was working gave no trace of the sodium spectrum; nevertheless, after the introduction of chlorate on the end of a loop of fine platinum wire recently heated to redness, the sodium line was seen, though very faintly.

Several grms. of this chlorate were reduced to chloride by the action of heat, and this was volatilised by the method mentioned above. When it was reduced to about 1-100th of its original volume, the residue began to form very weak concentric rings of silicate fusible at the highest temperature. On carrying volatilisation to completion, the chloride was evaporated *without depositing any brilliant specks, though a series of rings, very thin, colourless, transparent, and very fusible, was deposited.* These little rings, when heated in the oxyhydrogen blowpipe, gave it a *violet* colour. Spectrum analysis of the flame enabled me to detect the presence of the sodium line, side by side with the potassium spectrum, but the characteristic calcium lines were entirely absent, although the temperature was high enough to melt the platinum in which the chloride was volatilised.

In face of this result I repeated the solution and crystallisation of the chlorate in water containing one per thousand of hydroxide of potassium, made from nitre as pure as I could get it. I washed the salt first in this same alkaline iced water, and then with pure iced water, working, as I have mentioned above, in a large room *apart from the laboratory.*

The chlorate from this *fifth* treatment coloured a Bunsen flame *pure pale blue,* and on spectrum analysis of the flame I could not see the sodium line any stronger than in air without chlorate.

I once more reduced part of the salt to chloride. Its dissociation was effected without evolving chlorine. Ten grms. of absolutely colourless and *neutral* chloride were volatilised without leaving a trace of residue visible under the microscope,

Fearing, nevertheless, the presence of traces of dust and alkali in this salt, I made the solution in almost boiling pure water, and I passed the saturated liquid through small filter-papers, in platinum funnels, purified with water acidulated by hydrofluoric and hydrochloric acids, and then with pure water. The filtered liquids were received into platinum vessels, *all of which were placed on smooth sheets of glass, and covered with a bell-jar, with a ground and polished edge and with its surface moistened,* to stop contamination by dust.

After filtration and carefully washing the filters with water, I was unable to detect on the surface of the paper the slightest trace of dust, or any deposit whatever.

The filtered solution, which was no longer saturated a

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* The preparation of a solution of hydroxide and sulphydrate of potassium, as free as possible from sodium, is a very delicate operation. I procured the compounds used in my researches by means of oxide of potassium made by Wöhler's method,—that is to say, by heating a mixture of nitre and pure copper in excess, in a large copper crucible made by electrolysis from pure sulphate of copper. The nitre came from nitrate purified for powder-making. I crystallised it *three times* in a one per thousand solution of sulphydrate of potassium, *seven times* in a one per thousand solution of hydroxide of potassium, *working in enclosed and purified air,* in a large platinum retort, and finally *twice* in pure water. The nitrate, which was crystallised three times in the sulphydrate converted into chloride, was *completely* volatilised; but when put into a flame it showed, on spectrum analysis, the sodium line with a comparatively great intensity. It therefore still contained some sodium, without doubt in the form of a nitrate. After having crystallised it *four times* more in water made alkaline by hydroxide of potassium, and *twice* in pure water, it gave the flame a blue tint slightly tinged with violet, and showed the sodium line *very faintly* until it was completely volatilised, which was done with very great rapidity. I must confess that when working with nitre already purified I was not able to prepare nitrate of potassium *absolutely* free from sodium by means of successive crystallisations in alkaline and pure water. But, judging by the faintness of the sodium line, the amount of sodium held by the nitre did not exceed the amount often found in *dry* air, when undisturbed for eighteen hours in a very large room. The solution of hydroxide of potassium resulting from the absorption of water by oxide of potassium always contained copper, owing to the action of copper on nitre. The separation of copper from the solution was effected by means of a proper quantity of hydrosulphuric acid. The transformation of hydroxide free from copper into sulphydrate, and the preservation of the hydroxide and sulphydrate solutions, are done in closed platinum vessels, to protect them from contact with the air.

boiling-point, was put back into the large platinum crucible, the neck of which reached very far into a flask, and was concentrated down almost to dryness, and then quickly cooled. The mother-liquor, although colouring a flame pale blue and *not showing the sodium line*, was entirely separated. The chlorate was dried in the platinum crucible covered by a lid, the long neck of which reached far into a flask full of purified air, by placing the crucible in an air-bath heated to 100°.

Out of *five kilogrms.* of commercial salt, worked upon in two operations, I only saved *four hundred grms.* of chlorate that I could consider pure,—that is to say, only *eight per cent* of the weight of salt used.

I made, with the greatest care, an experiment on the chlorate obtained in each operation, to ascertain the quantity of solid matters left after evaporating the chloride made by dissociating it in a covered platinum retort. I took 5·007 grms. of chloride from the first chlorate, and 8·190 grms. of chloride from the second chlorate; in both cases the material experimented upon was volatilised *without leaving a trace of residue, I do not say "weighable," but not even visible under the microscope.*

These two researches, the execution of which was as laborious as delicate, enable me to state that under suitable conditions, it is possible, contrary to my previous opinion, to obtain chlorate, and therefore chloride, of potassium *absolutely* free from sodium and solid matters.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Special Meeting, December 13th, 1895.

Prof. **Reinold**, Vice-President, in the Chair.

The Resolution with reference to the change in the amount of the life-composition fee, passed at the Special General Meeting held on November 22nd last, was confirmed.

The Ordinary Meeting was then held.

Dr. **John Shield** read a paper on "*A Mechanical Device for Performing the Temperature Corrections of Barometers.*"

The form of barometer to which the author has adapted his device is that devised by Dr. Colley; it is intended for general laboratory use, and is capable of being read to within 0·1 m.m. The barometer tube can be moved in a vertical direction, so that the lower meniscus can be adjusted to the zero of the scale. Attached to the barometer tube is a thermometer with a horizontal stem, passing in front of a scale which is fixed to the vertical scale of the barometer. The graduations of this thermometer scale, with the exception of the one passing through the 0° C. mark on the thermometer, are inclined to the vertical, and are so spaced that the reading opposite the end of the mercury column of the thermometer gives directly the correction to be applied to the observed height of the barometer (B_t) in order to obtain the reduced height (B_0); that is, the reading on the thermometer scale gives the value of $B_t(\beta-\gamma)t$; where β and γ are the coefficients of expansion of mercury and of the material of which the barometer scale is composed respectively, and t is the temperature.

Mr. **Boys** admired the simple method the author had adopted for plotting the corrections, and said that he always felt that the trouble involved in applying small corrections ought, if possible, to be avoided, or the corrections would often be omitted.

Mr. **Appleyard** advised the placing of the bulb of the thermometer within the barometer tube.

Dr. **Shield**, in his reply, said as the barometer was only intended to read to 0·1 m.m., the placing of the thermometer within the tube did not appear necessary.

A paper by Prof. **Rücker** on "*The Resistance of Vertical Earth-air Currents in the United Kingdom*" was, in the absence of the author, read by Mr. **Kay**.

In a paper read before the British Association, at Oxford, Dr. Schmidt stated that he had expanded the components of the earth's magnetic force in series, and had deduced expressions, two of which give the magnetic potential on the surface of the earth, in so far as it depends on (1) internal and (2) external forces. "The third series represents that part of the magnetic forces which cannot be expressed in terms of a potential, but must be due to electric currents traversing the earth's surface."

Dr. Schmidt concluded that such currents amount on the average to about 0·1 ampère per square kilometre. The author has tested this conclusion, drawn from the state of the earth as a whole, by means of an examination of the line integral of the magnetic force round a re-entrant circuit, taken in the United Kingdom. The necessary data have been obtained from the results of the magnetic surveys for the epochs 1886 and 1891, carried out by the author and Dr. Thorpe. Two circuits called the α and β circuits were selected, having their greatest extension north and south and east and west respectively. The work done by a unit magnetic pole on traversing these circuits was calculated for the epoch 1886 by means of the terrestrial lines found for that date, and also for the epoch 1891 by means (1) of the same lines when due allowance was made for secular change, and (2) of the independent set of lines found by aid of the 1891 survey. The same calculation was made for a third circuit (γ) using, instead of the calculated terrestrial lines, the true values of the forces and delineations as deduced from the nearest stations. The following table gives the results in ampères per square kilometre:—

	α.	β.	γ.
1886	−0·026	−0·004	—
1891 (1)	+0·001	−0·005	—
1891 (2)	—	—	−0·008

From these figures the author concludes that there is not, in the United Kingdom at any rate, a vertical current amounting on the average to 0·1 per square kilometre.

Mr. **Watson** said a few words on the difficulty experienced in determining the line integral in South Wales, due to the presence of closed curves.

The Society then adjourned till January 24th, 1896.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Second Ordinary Meeting, Monday, December 2nd, 1895.

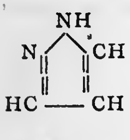
Dr. **Mackenzie** in the Chair.

Dr. Macdonald read a paper on the "*Constitution of Pyrazole*," being an account of the work done by himself at Jena, of which the following is an abstract.

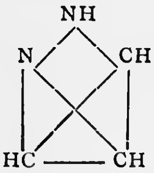
It was pointed out that three constitutional formulæ had been proposed for pyrazole, and these by Knorr, Buchner, and Bamberger, modelled on the benzene formulæ of Kekulé, Claus, and Baeyer respectively. For derivatives with a substituting atom or group on one of the nitrogen atoms an unsymmetrical formula accounts for all observed phenomena; but otherwise, according to results obtained by him in the Chemical Laboratory at Jena, each of the above-mentioned formulæ is inapplicable.

A methylpyrazole, necessarily 3- or 5-methylpyrazole, which showed no trace of isomers, was prepared synthetically. Next both 3- and 5-methylpyrazole were prepared analytically by burning away, by means of permanganate of potash, the phenyl-group from 1-phenyl-3-methylpyrazole and 1-phenyl-5-methylpyrazole respectively—a reaction which was found to go better on the introduction of a nitro-group into the benzene ring, and subsequent reduction. These analytically prepared substances were both identified with the synthetically prepared methylpyrazole by the boiling-point and by the preparation of four derivatives—the corresponding pyrazole carboxylic acid and nitromethylpyrazole, and the double salts with $AgNO_3$ and $HgCl_2$. Of some twenty derivatives of the synthetical product, these four had been selected as the best adapted for the identification.

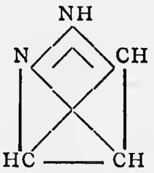
According to this result, the molecule is synthetical, and each of the three formulæ—



Knorr's.



Buchner's.



Bamberger's.

is impossible.

The difficulty of disposing of the H atom, which in the above formulæ is attached to a nitrogen atom, makes it hard to say what the correct formula may be. It seems that this H atom must move from atom to atom in the ring. As to whether it visits every atom in the ring, or only the two nitrogen atoms and the middle carbon atom, or the two nitrogen atoms merely, cannot at present be decided.

Third Ordinary Meeting, Monday, December 9th, 1895.

Dr. Mackenzie in the Chair.

Dr. Marshall read a paper on "*Optical Activity and Crystalline Form*," of which the following is an abstract.

In an ordinary ray of light the vibrations take place successively in all possible directions perpendicular to its axis. By certain means it is possible to restrict the vibrations to one particular plane. The ray is then said to be plane-polarised.

This may be accomplished by means of certain crystals, such as calc-spar or tourmaline, which have the property of double refraction.

While studying the action of plane-polarised light on crystalline plates, Arago noticed that a plate of quartz cut at right-angles to the optic axis, rotates the plane of polarisation of light transmitted through it. He further noticed that some specimens of quartz rotate the plane of polarisation to the right, and some to the left. This remarkable phenomenon was carefully investigated by Biot, who deduced the following laws:—

1. The amount of rotation is proportional to the thickness traversed by the ray.
2. The rotation effected by two plates is the algebraic sum of the rotations produced by each separately.
3. The rotation is approximately proportional to the inverse square of the wave-length of the light used.

Biot soon discovered that many organic liquids, solutions, and vapours also rotate the plane of polarisation.

It was soon noticed that the optical activity of crystals was a quite distinct phenomenon from the optical activity of liquids. Thus Herschel, by dissolving quartz in fused potash, found that the optical activity disappeared. Herschel also observed that there was a connection between the direction of rotation and the arrangement of the plagihedral faces on quartz crystals. Here the optical activity is due to crystalline structure.

In the case of liquids, solutions, and gases, Biot's experiments on oil of turpentine showed that here the optical activity is due to individual molecules.

Substances which are optically active only in the solid state, such as quartz, sodium chlorate, sodium bromate, Schlipp's salt, cinnabar, &c., are without exception isotropic or uniaxial. Substances which are optically active only in the liquid state, such as tartaric acid and its salts, are all compounds of carbon.

Pasteur carefully investigated the two optically active tartaric acids. When in solution, they rotate the plane of polarisation equally, but in opposite directions. The crystals are hemihedral and enantiomorphous; though this is the case with all optical isomers, the converse is not true, since many substances are known which, though crystallising in forms devoid of planes of symmetry, are not optically active in solution.

Some substances, such as strychnine sulphate and rubidium tartrate, are optically active both in the crystalline state and when dissolved.

Wyrouboff has studied numerous allied compounds, and has tried to apply Mallard's theory of the rotatory power of crystalline substances to solutions. He arrives at the following conclusions:—

1. That the rotatory power of substances in solution, like the rotatory power of crystalline bodies, depends on the structure of the crystalline molecule, as distinguished from the chemical molecule.
2. In solution the crystal molecules are not broken up, and therefore there can still less be dissociation into ions.

CORRESPONDENCE.

ON THE PLACE OF HELIUM IN THE CLASSIFICATION OF ELEMENTS.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lxxii., p. 291) Mr. Wilde accuses me of loose arithmetic and looser assertions. This charge is founded on a short report of some extempore remarks which I made at the Physical Society on November 22nd, during the discussion of a paper by Dr. Johnstone Stoney.

My first impulse on reading that report was to write a letter explaining that it was inaccurate. On second thoughts I refrained, for the arithmetical mistakes were so obvious that I thought every reader who knew anything of the subject would put them down as a reporter's or printer's error. The figures given were certainly not those which I wrote on the black board. If they had been correctly given there would have been little difficulty in understanding my previous statement, notwithstanding its very condensed nature.

My object was to show that if the two new gases of which helium is probably composed are really analogous to the alkaline metals, as Prof. Runge's photographs of the spectra seemed to indicate, there was no serious difficulty in placing them in the same group. It is evident that the difference of atomic weight between hydrogen and lithium is only 6; between lithium and sodium it rises to 16; and after two terms it again rises to 24. Subsequently it is probable that the difference is still further increased. There would therefore be no difficulty in supposing that the first difference might be less than 6.

Excepting in their bearing on the position of helium, the views expressed by me are by no means new. As far back as 1853 I showed (*Phil. Mag.*, May, 1853) that the atomic weights of several series of analogous elements differed by certain increments like those in the well-known organic series, and I drew special attention to the occurrence of the numbers 16 and 24. In an address to the Chemical Section of the British Association, in 1883, speaking of the atomic weights in Mendeleeff's table, I observed that "those in the vertical series differ from one another, as a rule, by the before-mentioned multiples of 8, namely, 16, 16, 24, 24, 24, 24, 32, 32, the elements being generally analogous in their atomicity and in other chemical characters."

I have no desire to discuss Mr. Wilde's ingenious speculations, whether in his paper of 1875 or that of 1894; and, as far as the position of helium is concerned, it would seem desirable to wait for further light on its nature.—I am, &c.,

J. H. Gladstone.

17, Pembridge Square,
November 17, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 22, November 25, 1895.

M. Launelongue has been elected a Member of the Section of Medicine and Surgery, *viee* the late M. Verneuil.

On Para-ethoxyquinoleine. — C. Grimaux. — The author describes the preparation and properties of quinethol, $C_{11}H_{11}NO$, its hydrochlorate, sulphates, and nitrate. Quinethol is a weak base; its salts with the organic acids are dissociated by water. By dissolving quinethol in sulphuric acid and adding two mols. of fuming nitric acid we obtain nitroquinethol, $C_{11}H_{10}(NO_2)NO$. It has feeble basic properties. Amidoquinethol, $C_{11}H_{10}(NH_2)NO$, is obtained by reducing the nitro-compound with stannous chloride in a hydrochloric solution at a temperature below 50°. It is easily diazotised, and yields tinctorial diazo-compounds. Quinethol has no action upon intermittent fevers, and has no anti-periodic properties.

Rapid Determination of Nitric Nitrogen in Vegetable Substances.—P. Pichard.—This paper will be inserted in full.

Action of Phenol upon Mercurous Iodide.—Maurice François.—At the temperature of ebullition the decomposition of mercurous iodide by phenol is limited by the quantity of mercuric iodide existing in solution. The decomposition always ceases when 100 parts of liquid contain 2·75 grms. mercuric iodide. In presence of metallic mercury if a solution of mercuric iodide in phenol contains more than 2·75 grms. of mercuric iodide in 100 grms. of solution, there is found mercurous iodide.

Manganese Silicide.— M. Vigoureux.— Manganese silicide has a metallic lustre, and is very hard, brittle, and perfectly crystalline. Its specific gravity at 15° is 6·6. It is unalterable in air and fusible in the reverberatory furnace. Fluorine attacks it at the ordinary temperature, forming white fumes of silicon fluoride. If heat is applied there ensues combustion, with flame and incandescence. Dry chlorine acts at 500° with lively incandesccence, silicon chloride being evolved. Iodine and bromine react less readily. Caustic potassa with the aid of heat attacks this compound energetically. Its composition is $SiMn_2$.

Toxicity of Acetylene. — L. Brociner. — Acetylene exerts merely a very feeble poisonous action, not more marked than that of the ordinary hydrogen carbides, such as formene, ethylene, or propylene. Animals exposed to the action of mixtures containing considerable proportions of acetylene for several hours do not succumb if we are careful to operate in presence of a considerable quantity of oxygen, and to renew the gaseous mixture so as to prevent the products of the animal's respiration from accumulating.

Some Reactions of Tartaric Acid and the Alkaline Tartrates.—L. Magnier de la Source.—If to a concentrated solution of potassium acetate we add a relatively small proportion of tartaric acid (though more than sufficient to precipitate with an equal volume of solution of potassium sulphate) there is no immediate precipitate. The addition of a mixture of ether and alcohol renders the precipitation more rapid, and the addition of acetic acid renders it immediate.

Presence of Laccase in Fungi.—Em. Bourquelot and G. Bertrand.—Laccase exists not merely in green plants, but in such as are devoid of chlorophyll.

Distribution of the Nitrogenous and Mineral Substances in Bread.—There exists no more nitrogenous and saline matter in the crust of bread than in the crumb if both are brought to the same degree of dehydration. The baking of bread does not effect any destruction of matter. There is a loss of fatty substances and an increase of saccharine matter, but the total weight does not vary to an appreciable extent. Dry bread does not contain more nutritive matter than the dry flour used in its production.

MISCELLANEOUS.

Corrugated Packing Paper and Boards.—We have received, from Messrs. Bracht and Friedlaender, specimens of an improved packing material which they are introducing to the English market. From a careful examination we think that its use will be found very convenient and safe for packing breakable goods, as well as for forwarding samples for analysis, specimens of dry colours and other fine chemicals, electros for the illustration of books and journals, &c. The double corrugated paper is calculated to supersede other materials as an enclosure for phials, specimen tubes, and glasses, as it combines lightness with great resistance to pressure and concussion. It is manufactured in a variety of colours and shapes adapted for various purposes.

NOTES AND QUERIES.

Glass Cloth for Acid Filtering.—Will some reader kindly state where the article known as glass cloth for acid filtering purposes can be obtained, and who are the manufacturers?—W.

TO CORRESPONDENTS.

H. F. J.—We are of course aware of the two views you mention concerning the electrodes in voltaic cells; but we cannot trace who is originally responsible for each opinion.

THE CHEMICAL NEWS.

Vol. LXXII., No. 1883.

INVESTIGATIONS OF THE CHEMICAL HISTORY OF THE BARLEY PLANT.*

By C. F. CROSS and CLAUD SMITH.

It is becoming evident that useful research in matters agricultural must henceforth take the form of physiological diagnosis. The investigation of crops in relation to soils and fertilisers has of course rendered incalculable service, and in this country the distinguished group who have presided over the Rothamstead Experimental Station have done much to lay the foundation of sound scientific practice. At this date, however, we have to confess that the fundamental problem of *Assimilation* is, so far as the agriculturist is concerned, so much "virgin soil." While experience and the vast accumulation of observations furnish more or less accurate impressions of the results of the process, the process itself is one of those factors of production which are still "taken for granted." We may except, perhaps, from this general statement certain positive results which have followed the application of methods of selection based upon observation of variations of particular products of assimilation, such as the improvement of the sugar beet in relation to the production of sugar. But even here the methods pursued are empirical and involve no consideration of the actual mechanism of assimilation.

Now that methods of more exact proximate resolution of mixtures of carbohydrates are in our hands, the time has arrived for their application to growing crops as the necessary basis of a knowledge of the course of assimilation, or more generally of the chemical life history of the plant. It would be out of place to prejudice the enquiry by asking what are the useful results likely to follow from such investigations. It must be positively assumed that such results will certainly issue, and the work must be begun upon the conviction.

On this view we have carried out for two years periodical investigation of barley crops growing upon the experimental plots of the Royal Agricultural Society at Woburn. We selected two plots giving respectively the minimum and maximum yields of grain over a succession of years, viz.—

Plot 1. Permanently unmanured.

Plot 6. Manured with 200 lbs. sulphate of potash, 100 lbs. sulphate of soda, 100 lbs. sulphate of magnesia, 3½ cwts. superphosphate of lime, and 275 lbs. nitrate of soda.

Our observations have been chiefly directed to the cellulosic basis of the straw. It has been previously shown that the celluloses of cereals are widely differentiated from the normal type in the presence of a large proportion of furfural yielding constituents. While there are in part pentoses or pentosan groups, they consist in the main of oxidised derivatives of the hexoses; and being the most characteristic constituents of the permanent tissue it was clearly necessary to study the history of their assimilation as the basis of a systematic investigation of the history of the plant.

We now give without further preliminary explanation the actual experimental numbers arrived at, as the scope of the investigation will be grasped from a mere inspection of the tables of figures.

In reference to the methods of observation, the results of which are embodied in the table, it is perhaps necessary to explain what is meant by "permanent tissue." The plant may be regarded as made up of cellular and fibrous tissue, cell contents, and excreted products. To eliminate the latter and isolate the tissue the following process has been employed:—

1. After reducing the plant to "chaff," exhaustive extraction with boiling alcohol. 2. The residue is digested

Barley Samples.—Woburn.

		Plot 1.—Minimum Yield.			*Plot 6.—Maximum Yield.*			
Date.	Age of Crop.	Plot.	Total Dry Matter. Per cent.	Furfural. (*a*) Per cent of dry weight.	Permanent Tissue. P.c. of dry weight.	Furfural from Permanent Tissue. (*b*) P.c. on tissue.	Furfural from Permanent Tissue. (*c*) P.c. on total.	Ratio.
1894. May 7.	6 weeks	1	19·4	7·0	53·4	12·7	6·8	1·03 : 1
		6	14·7	7·0	55·9	10·3	5·7	1·23 : 1
June 4.	10 weeks	1	17·6	7·7	52·9	11·6	6·1	1·26 : 1
		6	13·5	8·1	58·5	13·4	7·8	1·04 : 1
July 10.	15 weeks	1	42·0	9·0	65·7	9·8	6·4	1·40 : 1
		6	32·9	10·6	65·7	12·5	8·2	1·30 : 1
Aug. 21.	21 weeks	1	64·0	11·9	70·0	14·5	10·1	1·18 : 1
		6	64·6	13·4	70·5	15·0	10·6	1·26 : 1
Aug. 31.	22 weeks 3 days.	1	84·0	12·7	75·0	16·5	12·4	1·02 : 1
		6	86·4	12·4	78·4	15·1	11·8	1·05 ; 1
1895. May 15.	7 weeks	1	20·6	6·6	53·9	10·2	5·5	1·20 : 1
		6	17·8	5·8	56·7	9·6	5·4	1·07 : 1
June 18.	12 weeks	1	34·6	8·0	38·2	14·7	5·6	1·42 : 1
		6	33·4	7·6	44·5	15·0	6·7	1·14 : 1
July 16.	16 weeks	1	52·8	12·1	55·6	16·3	9·1	1·33 : 1
		6	54·4	10·6	46·2	19·1	8·8	1·20 : 1
Aug. 16.	20 weeks	1	66·8	9·2	49·1	17·0	8·3	1·10 : 1
		6	65·0	9·8	49·8	19·1	9·4	1·04 : 1
Sept. 3.	22 weeks 4 days	1	84·8	10·4	45·7	17·6	8·0	1·31 : 1
		6	86·3	10·2	45·3	17·3	7·8	1·30 : 1

Note.—The experimental results are expressed throughout upon the *whole plant*. For the agricultural bearings of the numbers it is necessary to further analyse the later numbers in reference to grain and straw. These points will be dealt with elsewhere. Our scheme of experiments for 1896 includes an examination into the effects of preventing the formation of seed upon the permanent tissue of the stem.

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* Read before the British Association (Section B), Ipswich Meeting, 1895.

four hours at the ordinary temperature with dilute caustic soda (2·0 per cent NaOH) and then washed, at first with cold, lastly with boiling water. 3. The residue is then digested with dilute hydrochloric acid (2 per cent HCl) in the cold, and then washed with cold, lastly with boiling water.

The residue we take as approximately representing the tissue constituents. The process being one of hydrolysis is of empirical and somewhat arbitrary value. The value of the results will be estimated by their own internal evidence. If the definition "permanent tissue" be objected to, it is easy to substitute the more correct description, which is "the residue from treatments by chlorophyll solvents and by hydrolytic agents, alkaline and acid, under carefully regulated conditions." The product has served the purposes of these investigations, and will, we think, be seen to have the value of a "constant."

We draw a number of conclusions from the result:—

1. The conditions of soil nutrition are seen to have very little influence upon the composition of the plant. Comparison of the numbers for the two plots taken in pairs show certain fluctuations, it is true, and these are most marked at the most active period of growth, *i.e.*, at the flowering stage. Contrasted with this, the final condition of the tissue, *i.e.*, at maturation, may be taken as identical under conditions of minimum and maximum soil nutrition, as it may also at the initial stages of germination and early growth. The plant, in other words, is, as regards soil nutrition, constant or invariable in respect of the relation of its products of assimilation.

2. If we had had the selection of extreme variations of season we could not have chosen better than as between 1894 and 1895. The influence upon the experimental numbers is extreme, more especially in regard to "permanent tissue." In the comparatively wet season of 1894 there is a steady increase of permanent tissue; in 1895 the brilliant and continuous sunshine of the period up to and including that of flowering determined a totally different course. The proportion of easily hydrolysable carbohydrates shows a steady increase during the maturation period *at the expense of permanent tissue.* The *total dry matter*, on the other hand, was influenced only in the stages up to and somewhat after the flowering period. *Dehydration* was for obvious reasons much more active in 1895, and the difference of condition in this respect in the case of plot 6 is quite remarkable. Certain industrial consequences follow from the history of the tissues (see foot-note to table): (1) the *feeding value* of straws grown in dry seasons is high: and (2), conversely, the *paper-making value* of such straws is low. Moreover, while we may well assume a diminishing feeding value of the 1894 straw during the period of maturation, it would appear that in 1895 there is an actual increase of feeding value of the mature straw over the straw taken at the flowering period. It is of course to be admitted that artificial hydrolysis is only a crude measure of digestibility, and it would be important to confirm the conclusion by actual feeding experiments. That must be deferred to future opportunities.

3. The furfuroids have been diagnosed in various ways, chiefly with the view of determining their distribution as between hydrolysable and non-hydrolysable (permanent tissue) constituents. In the early and late periods of growth the furfuroids are in the main of cellulosic character. The greatest divergence is seen to occur at the most active period of growth, and here there is an accumulation of easily hydrolysable furfuroids. The maximum proportion was similar in the two seasons; in both crops there is a gradual rise to and falling from the maximum; in the 1895 crop there was a marked change after cutting, and the change in the character of the furfuroids was accompanied by a retrograde change in the "permanent tissue." This retrograde movement, it will be noted, was continuous from the flowering period and in exact contrast to the history of assimilation in 1894.

A fair interpretation of the results appears to be this: the furfuroids are by no means excreted products, but available for assimilation, and they are in fact continuously assimilated to permanent tissue (cellulose). Owing to the deficient moisture in the period to July 16th the building up of new matter (growth) was interfered with, and the "permanent tissue" was put under contribution for nutrient material which, under ordinary conditions, would have been drawn from *cell-contents* and not from tissue.

In the month July 16th to August 16th there is, in fact, a notable falling off in the total quantity (proportion) of furfuroids, which confirms the view that these constituents were put under contribution selectively, to the general needs of the plant.

Viewed broadly and generally these investigations show how very different are the results of physiological study of the history of crops from those of investigations of soil nutrition. The essential characteristics of the plant are maintained independently of the factors of soil nutrition. The comparative study of the two crops proves this conclusively.

In our opinion systematic investigation of the actual physiological, *i.e.*, chemical, constants of the plant, will lead to results of which at present it is impossible to predict the import.

Take it that we had been able to make a complete proximate resolution of the straw substance from time to time, instead of confining ourselves to one group of the carbohydrate constituents: it is easy to see that much wider and more positive conclusions could have been drawn.

But private enterprise has its obvious limits, and exhaustive investigations of this character can only be undertaken by institutions fully equipped and supported by adequate funds.

We hope this preliminary contribution will serve as an indication of the results likely to follow from the systematic work of such an institution.

ON THE

PERCENTAGE OF ARGON IN ATMOSPHERIC AND IN RESPIRED AIR.[*]

By ALEXANDER KELLAS, B.Sc.,
Assistant in the Chemical Department of University College, London.

Although blood invariably contains a small amount of dissolved nitrogen, it appears that with animals no absorption of that gas takes place than what is due to its solubility in the serum of the blood. Nor is nitrogen eliminated from the system in the elementary state.

At Professor Ramsay's suggestion, experiments have been made on the comparative amount of argon in ordinary air, and in air which had been frequently breathed, with the view of ascertaining whether, if the proportion of oxygen and carbon dioxide in air be very much altered, argon would either enter into, or be expelled from the respiratory system. The result of the experiments to be described is to show that the proportion of argon to nitrogen remains nearly normal, even when the air has been greatly altered in composition by respiration.

1. *Percentage of Argon in Atmospheric Air.*—A mercury reservoir, the capacity of which was accurately determined by weighing with water, held 555·2 c.c. The upper end was fitted with a three-way tap, sealed on to the glass. Through this tap was admitted air, purified by passage over soda-lime and phosphoric anhydride, to remove water-vapour and carbonic anhydride. This reservoir was jacketted with water of known temperature, so that the volume of the air could be measured with great exactness. The other branch of the three-way tap led to a tube filled with copper, in order to absorb oxygen; one

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[*] A Paper read before the Royal Society.

containing copper oxide to destroy any organic matter which might have been present, and one filled with magnesium turnings to absorb nitrogen; these tubes were kept red hot. Other tubes were filled with soda lime and phosphoric anhydride, so as to remove water and carbon dioxide, which might have been produced. The air was circulated over these absorbents until little but argon was left. The gas-holder was filled three times at 18·8° C., and 752·1 m.m. pressure. After absorption had nearly ceased, the remaining gas was pumped out of the tubes, mixed with oxygen, and sparked for many hours in presence of caustic soda, to remove the last traces of nitrogen. The residue, after absorption of oxygen with potassium pyrogallate, measured 15·91 c.c. at 21·4° C., and 754·5 m.m. pressure.

Reducing both volumes to standard temperature and pressure, it appears that—

1542·0 c.c. of air yielded 14·45 c.c. of argon, or
100·0 c.c. of air contain 0·937 c.c. of argon.

Calculating the percentage in atmospheric nitrogen, we have—

100 c.c. of mixed atmospheric nitrogen and argon contain 1·186 c.c.

Owing to the avoidance of the presence of water during these experiments, they are probably more accurate than the original experiments of Lord Rayleigh and Professor Ramsay. They found ("Argon," *Phil. Trans.*, 1895, A, pp. 221 and 214) 1·04 and 1·03 in two experiments in which the nitrogen was removed by sparking with oxygen in presence of dilute caustic soda; and 1·11 when the nitrogen was removed by means of magnesium.

Owing to the vacation, it has not been possible to put this result on record before now. And Th. Schlœsing, jun., has recently published *Comptes Rendus*, vol. cxxi., p. 605) the results of a series of estimations in which the percentage of argon in atmospheric nitrogen was found to be 1·180 to 1·185, or as a mean 1·183 per cent, a number almost identical with that just recorded. M. Schlœsing has re-calculated the ratio which ought to subsist between the densities of atmospheric and "chemical" nitrogen on the basis of his determinations; but in doing so, he has made use of the value 1·2505 grm. as the weight of one litre of the latter, instead of 1·2511 (*Phil. Trans.*, 1895, A, p. 189). Moreover, he has assumed Regnault's value, now superseded, for the weight of 1 litre of hydrogen, viz., 0·0896 grm., instead of that given by the more recent determinations, 0·0899 (*Phil. Trans.*, 1895, A, p. 292). These are not serious errors, but it is more satisfactory to calculate the correct number. The question is:—If the weight of a litre of pure nitrogen is 1·2511 grm., and of argon 1·7818 grm., and if atmospheric nitrogen contain 1·185 per cent of argon, what should be the weight of a litre of the latter? The answer is 1·2574. Lord Rayleigh found the number 1·2572, one almost exactly identical.

For material for the second part of this research, I have to express my thanks to Dr. Marcet, F.R.S., and his assistant, Mr. Floris. The air was analysed before having been breathed, and had the normal composition:—

Nitrogen and argon.. ..	79·02	per cent
Oxygen	20·93	,,
Carbon dioxide..	0·05	,,
	100·00	

The air was breathed over and over again by Mr. Floris, until after ten minutes' respiration its composition had become:—

Nitrogen and argon.. ..	80·96	per cent
Oxygen	5·40	,,
Carbon dioxide..	13·64	,,
	100·00	

An estimation of the argon was carried out in precisely the same manner as before, on 1297·8 c.c. of breathed air, measured at 17·2° C. and 759 m.m. pressure. But the air was breathed over water, the requisite change of volume on respiration having been secured by breathing into one of Dr. Marcet's counterpoised gas-holders. The argon found measured at 17·7° C. and 752·3 m.m. pressure 12·85 c.c. These numbers corrected give—

1196 c.c. of breathed air yielded 11·72 c.c. of argon.
100 c.c. ,, ,, 0·980 c.c. of argon.

Calculating the percentage on the nitrogen, we have:—

100 c.c. of nitrogen and argon of breathed air contains 1·210 c.c.

This percentage is larger than that in normal air. One of two suppositions may be made:—Either the increased amount is due to the air having been confined over water during breathing, or argon is given off from blood in greater amount than it is absorbed, when the composition of the air in the lungs is so much altered; the former appears the more probable supposition. In any case the difference is not great; and it would appear that argon, like free nitrogen, plays no important part in the animal economy, save as a diluent.

ON THE

ORIGIN OF THE ARGON AND THE HELIUM IN THE GASES ESCAPING FROM CERTAIN SULPHUROUS SPRINGS.

By L. TROOST and L. OUVRARD.

In his communication concerning the presence of argon and helium in the gases liberated from the sulphurous springs of Cauterets, Dr. Bouchard has indicated the importance of examining, from the same point of view, the gases in solution in waters which flow or stand on the surface of the ground.

We might, in fact, put forward the idea that the gases liberated by the sulphur waters are derived exclusively from the atmosphere. The solubility of argon might cause us to admit that the gases carried down by the waters from the surface into the depths of the earth, re-ascend with the same waters which have been rendered alkaline by a sulphide.

To throw a light on this question we have examined the gases from the water of the Seine (supplying the laboratories of the Sorbonne), and from sea-water, collected at high tide on the shore of the ocean. We have there sought for helium, independently of argon, which we were certain to find, since it is more soluble than nitrogen, which always exists in waters in contact with the atmosphere.

These gases, collected with the ordinary precautions and freed from carbonic acid by means of potassa, were treated in two different manners. The nitrogen was removed either by causing it to be absorbed by magnesium heated to redness, or by combining it with oxygen under the influence of electric sparks in presence of potassa.

This latter procedure is more tedious but more trustworthy, since the gas, constantly enclosed in the same glass tube over mercury, and without any transferences, is preserved from any mixture, even with very minute quantities of atmospheric air.

The gaseous residue obtained was dried over melted potassa and placed in connection, as in our former experiments (*Comptes Rendus*, cxxi., p. 394), with a Plücker tube with electrodes of magnesium in which a vacuum had been made by means of the mercurial pump.

The tube was repeatedly swept out with the gases in question, the vacuum being made each time anew. Then, after a final introduction of the gases, the effluve was caused to pass between the magnesium electrodes.

The spectroscope from the first constantly indicated the presence of traces of nitrogen, but on prolonging the experiment they disappeared. We were then able to decide that the spectra furnished by the gases from the wells of Cauterets were strikingly different from those afforded by the gases extracted from the water of the Seine and from sea-water.

These latter give the spectrum of argon, and merely traces of the spectrum of helium scarcely perceptible and often doubtful, whilst the gases collected at the well-head of the Baillière, or extracted by boiling the water from the same spring, give very distinctly the characteristic rays of argon and those of helium, and that the gases collected at the well-heads of the sources of the Bois give especially the characteristic rays of helium.

The helium contained in the gases liberated from the mineral springs of Cauterets does not consequently seem to us to be due to the atmosphere. The gas is derived probably from the rocks in the strata which these mineral waters have traversed.

The presence of helium lately proved in a certain number of minerals, such as clèveite, bröggerite, orangite, monazite, &c., renders this conclusion at least possible, so that, outside of any medical consideration, the study of the gases evolved by mineral waters would derive an especial interest from the fact that these gases may supply us with new information concerning the elements of the rocks which these waters encounter in the strata whence they issue.

With reference to the above communication, Dr. Bouchard added the following observations:—

I have stated in the paper to which M. Troost refers that, in all probability, the therapeutic activity of the mineral waters in which I showed the presence of argon and helium is not due to these gases. I added, that if these gases were present in the waters which flow or stand on the surface of the earth, the question would be decided, since these (surface) waters have not the therapeutic value of the mineral springs in question. But if argon and helium are inert, it may not be the same with mineral substances with which they are in combination.

It is established, by the communication of M. Troost, that helium at least is derived from the depths of the waters. Among the mineral compounds of helium there may be some which, even in minimal cases, may exert a physiological action upon the organism. On this hypothesis the effect would be due not to helium, but to the metal with which it was combined, always supposing that such a compound or its derivatives were sufficiently soluble.—*Comptes Rendus*, cxxi., p. 798.

ON THE

PRESENCE OF ARGON AND OF HELIUM IN A SOURCE OF NATURAL NITROGEN.

By CH. MOUREU.

Quite recently M. Bouchard has pointed out the presence of helium in the gases of the springs of Bois (Cauterets), and that of helium and argon in the gases of the Raillière. Whilst studying the same subject, MM. Troost and Ouvrard have discovered an important property of argon and helium—that of being absorbed by magnesium at a very high temperature.

I have just recognised the same two elements together in another natural gas which escapes abundantly in large bubbles from the spring of Maizières (Côte d'Or). The water of Maizières is a lithium water containing a little calcium sulphate, and it has at the source the temperature of +12°. Thanks to the courtesy of M. Communaux, the director of the company, I have had at my disposal several litres of the gas. The specimens had been collected with all the usual precautions, so as to avoid contact with air, which would necessarily have introduced argon.

The analysis over mercury showed me at once that the gas contained a small proportion of oxygen (about 2 per cent), the residue presenting all the negative characters of nitrogen.

To detect argon and helium I had recourse to the kindness of M. Deslandres, who has kindly undertaken these delicate experiments. After absorbing the nitrogen by lithium at a dull red heat, the gaseous residue was introduced into Plücker tubes at a low pressure, and, on being submitted to the effluve, it gave the characteristic rays of argon and of helium.

We may add that the proportion of these gases has been found rather considerable; the volume of the gaseous residue not absorbed by lithium is between one-tenth and one-fifteenth of the total volume.

Although the analysis has not been carried further, it seemed to me interesting to communicate these results to the Academy, not only on account of the presence of argon and of helium in a source of natural gas, but because of the relatively high proportion of these two elements in the gaseous mixture.—*Comptes Rendus*, cxxi., p. 819.

THE MANUFACTURE AND COMMERCIAL SEPARATION OF GLUCINUM.

By H. N. WARREN, Research Analyst.

Probably one of the most eccentric metallurgical orders of the times has been recently executed at the Research Laboratory, in the method of manufacturing glucinum for jewellery purposes. In order to ensure a large percentage of glucinum in the ore selected, six pounds of emerald-dust and stones of dull water were specially imported from various parts of the world; ground to a fine powder, and the finer qualities separated by lixiviation and regrinding. The powder so prepared was next thoroughly incorporated with four times its weight of sodic carbonate, and finally fused for three hours at the highest temperature of a powerful blast-furnace, and afterwards cast into square plates for further treatment. The second operation consisted in dissolving the melt thus formed as near as possible by the aid of supersaturated steam; and further effecting a complete decomposition by the introduction of an excess of hydrochloric acid, and evaporating it to dryness in order to render insoluble the silica present.

The siliceous residue having been washed and squeezed in a suitable press, was now rejected; the washings, together with the filtrate, being rendered alkaline by means of an excess of sodium carbonate, the solution having previously been freed from iron and chromium by acetates, in accordance with the usual separation of these metals.

The precipitate obtained by the introduction of the sodium carbonate was now thrown into a commodious glass receptacle, and heated with an excess of gaseous sulphurous acid, in which both the alumina and glucina dissolve. The solution thus obtained, upon being raised to ebullition, precipitates the alumina in a granular form, in place of the tedious gelatinous deposit obtained by the old ammonia process, which in the former case is washed with the greatest of ease. To the second filtrate thus obtained was added an excess of ammonium carbonate, and the solution well boiled; the glucinum carbonate being thus completely precipitated, also in a granular form, and admitting of being readily washed. The precipitate thus obtained being further intimately mixed with an excess of lamp-black and ignited out of contact with the atmosphere, the mass thus obtained being afterwards converted into bromide by acting upon it with bromine-vapour at a full red heat in clay retorts. The bromide distils over, and is readily reduced to the metallic form by decomposing the same with an electric current of 12 volts 8 ampères.

The metal thus obtained, having been worked into articles, is now in the possession of the Ameer of Afghanistan.

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CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 304).

Preparation of Perchlorate of Potassium.

The chlorate of potassium, the preparation of which I have described above, is used for the preparation of pure perchlorate and chloride of potassium.

As I said above, my object was to decompose the chlorate in such a way as to make on, the one hand, the greatest possible quantity of perchlorate, and, on the other hand, a quantity of perchlorate just sufficient to make the chloride required to estimate its molecular relation to silver.

M. Marignac has published in his works the methods of obtaining this result, and to them I have nothing to add. I will confine myself to saying that I effected the reduction of chlorate into perchlorate and chloride in a large platinum retort, *the inside of which was first polished*, the neck on the lid of which entered into a large tube 50 c.m. long, containing a roll of asbestos packing, as I shall describe further on in a special memorandum.

The retort rested on an earthenware tripod, which was strengthened by iron wires; it was heated by means of a *single* Bunsen flame through two pieces of wire gauze, to distribute the heat evenly, which is *indispensable*.

I reduced it in four operations; two being for the purpose of getting from about 50 to 60 per cent of perchlorate of potassium, and two for getting 10 per cent only of this salt, entirely decomposing the chlorate experimented on.

The first operation was done at the lowest possible temperature, and occupied as much as twenty-six hours. I found that by keeping the fused chlorate at the temperature at which oxygen is slowly disengaged, and the vessel makes a noise or decrepitation similar to that heard when fresh water is heated beyond 80° in a metallic vessel, dissociation took place with an evolution of heat; the fused mass was eventually agitated, and finally became pasty. When it reached this state, all the chlorate was destroyed, and the maximum of perchlorate was obtained. The separation was effected without liberating a trace of chlorine, but the oxygen disengaged smelt of *ozone*. If, during the dissociation, which is exothermic, one does not sufficiently reduce the supply of heat, the mass heats itself until the platinum vessel becomes incandescent, as I have often found when reducing chlorate in a covered platinum crucible. In this case, not only does the chlorate decompose without forming perchlorate, but the greater part of the salt already formed decomposes, and leaves chloride only. This decomposition is, therefore, slightly explosive, and may, if one does not take care, cause the loss of part of the salt submitted to the action of heat. Whether the separation be made *slowly* or *quickly*, the chloride and perchlorate formed are white; there is no evolution of free chlorine, the chloride is neutral to litmus paper, and the platinum vessel is not altered at all.

I took the greatest pains to satisfy myself of these facts, as mentioned in the special memorandum on this subject, because, during my previous work, when working on siliceous chlorate, I always noticed a sensible evolution of chlorine, a very slight attack on the platinum, and the presence of this metal in the form of chloroplatinate in the chloride made.

I then turned my attention to obtaining the greatest possible quantity of perchlorate.

In two operations successfully carried on for this purpose, I warmed the chlorate to a temperature just sufficient to induce a *very weak* evolution of oxygen, and I kept the temperature constant from 8 a.m. to 6 p.m. for *two days and a half* consecutively, the length of time necessary to reduce the mass to a pasty condition, and obtain at the constant temperature the cessation of the evolution of oxygen, and the absence of very light fumes in the large long tube into which the neck of the retort lid entered.

To procure the perchlorate necessary for producing the amount of chloride required for estimating its molecular relation to silver, I noted the time required for the total decomposition, *at the lowest possible constant temperature*, of the perchlorate, effected by working on a mixture of almost equal weights of chloride and this salt, made from about 100 grms. of chlorate.

After oxygen ceased to be evolved at constant temperature—which is coincident with the complete dissociation of the chlorate, and the formation of the greatest amount of perchlorate compatible with this reaction—I gently raised the temperature until I caused once more a slight evolution of oxygen, and the appearance of the saline fume; I then kept the temperature constant for six hours. I found, by a preliminary trial, that at least twelve hours were required to decompose the whole of the perchlorate in the mixture at this temperature.

Separation of Perchlorate and Chloride of Potassium.

I effected this separation by dissolving the salt in pure cold water and using then just enough water to make a saturated chloride solution. Directly the chloride was dissolved, which was done in enclosed and purified air, the liquor coloured a Bunsen flame blue, though a *very much lighter* tint than chlorate gives. The solution was drawn off each time, and, although quite clear, it was poured into a filter-paper which had been most carefully washed with dilute hydrofluoric and hydrochloric acids and pure water, arranged in a platinum funnel covered by a bell-jar, the surface of which, as well as the glass plate on which it stood, was wetted. The solution was evaporated nearly to dryness in a loosely covered platinum dish, under a bell-jar filled with air saturated with moisture, so as to prevent, *as far as possible*, the *saturated* solution from rising up to the edge of the dish and depositing solid chloride on it.

The mother-liquor from chloride, crystallised by cooling, was *neutral* to litmus paper; it was drawn off into a platinum dish, and again evaporated down to saturation point under a damp bell-jar. The chloride deposited by cooling was separated from the mother-liquor, and this was evaporated to dryness under a damp bell-jar, carefully separating the chloride on the edge of the dish. By working thus, I obtained, in decreasing quantities, three samples of chloride made at the same time as the perchlorate.

I have most carefully examined the spectrum of each of these three samples, and found them to be identical.

I used the second sample to find out what residue it contained, and found none.

I shall describe further on how I treated each of these chlorides when estimating their molecular relation to pure silver.

Without removing the crystalline powdered perchlorate from the retort, I crystallised it three times, changing the mother-liquor and the water with which it was partially washed each time; they yielded a salt which coloured a hydrogen flame *pale* blue, and gave a potassium spectrum without the sodium line, similar to that of the chloride made at the same time as the perchlorate.

The boiling perchlorate solution, when put into a Bunsen flame on the end of a fine platinum wire spiral, coloured it a very pale blue. *Spectrum analysis did not show the sodium line.* This experiment was repeated several times—whenever the state of the air allowed it—and always with the same result.

I have plunged into this boiling perchlorate solution several fine platinum wire spirals, coated with spongy platinum, previously heated to redness. I have left them under a large bell-jar filled with the air of the room where I was working, for the purpose of showing to several people that pure perchlorate coloured a flame blue and had no sodium line in its spectrum. I found that after from twenty-five to thirty minutes the crystallised perchlorate on the platinum spiral had absorbed enough sodium from the air to show the sodium line, very faintly it is true, but still unmistakably. In fact, from the moment I left the spirals under the bell-jar, the air of the room, which took the place of the air in the bell-jar by diffusion, became charged with sodium owing to the draughts in the room. One must be well acquainted with all the difficulties met with in a research of this nature in order to get a true idea of them. I express myself more fully on this subject in my "Study of Atmospheric Air," to which I beg to refer my readers.

The perchlorate of potassium which had been crystallised three separate times in a platinum retort covered by its domed top, and filled with enclosed and purified air, was reduced to chloride in it. This decomposition, when carefully done, is not difficult; *the separation into chloride and oxygen was effected without evolving any chlorine, and the chloride was neutral to litmus paper.*

I treated the chloride made from perchlorate in exactly the same way as chloride made at the same time as this salt; that is to say, I put it into just sufficient cold water to dissolve it. The solution was passed through carefully cleansed filter-papers without leaving any residue after the filter was washed. The clear liquid was evaporated to saturation at 100°, in a platinum dish loosely covered with a sheet of the same metal, and under a damp bell-jar. The mother-liquor, when poured off from the crystallised chloride, was in its turn evaporated to saturation at 100°; and, finally, this last mother-liquor was dried in a loosely covered platinum dish under a damp bell-jar.

I have thus obtained three samples of chloride made from perchlorate under conditions which yielded by dissociation of chlorate, on the one hand, the greatest possible amount of this salt and the least possible of chloride; and on the other hand, one-sixth part, at the most, of perchlorate, and the rest chloride.

The second sample of chloride made from perchlorate was used for showing the spectrum of the metal in it. I found the spectrum to be *identical* with that of chloride made at the same time as the perchlorate.

Lastly, I have worked on three samples, in decreasing quantities, of chloride made by crystallisation during the course of an experiment undertaken for the purpose of studying the conditions to be fulfilled in order to *partly* decompose the perchlorate formed by the complete dissociation of the chlorate.

All these chlorides, when dissolved in water, gave *clear* solutions, *neutral* to litmus paper; nevertheless, when heated in a platinum dish with pure chloride of ammonium, *with an acid reaction*, to a sufficiently high temperature to evolve white fumes, they gave off vapour which turned red litmus paper distinctly blue.

Fearing that traces of sulphate of potassium were present in these chlorides, I submitted them all to special treatment.

Treatment of Chloride of Potassium by Pure Chloride of Ammonium.

All the samples of chloride of potassium mentioned above were melted in pure sal-ammoniac, which was prepared by passing ammonia and hydrochloric acid gases through pure water in a large platinum apparatus, supplying always an *excess* of ammonia. The gases were brought through purified rubber tubes, weighted with platinum to keep the open end down.

The solution, which smelt strongly of ammonia, was evaporated to saturation in the platinum apparatus. After cooling it quickly, the mother-liquor was poured off and entirely changed.

The chloride of ammonium left in the apparatus gave no *sodic reaction*—a proof that, under the above-mentioned conditions, neither the ammonia nor hydrochloric acid gas brought any trace of sodium. I emphasize this point, because the use of this sal-ammoniac to reduce oxides free from sodium into chlorides always forms compounds which give conclusive evidence of the presence of sodium *when these chlorides are hygroscopic.* I shall return to this subject when describing my researches on chloride of calcium.

Having found that sal-ammoniac, when separated, was quickly contaminated by sodium from the air, I sublimed part of it in a platinum retort *in an atmosphere of dry ammonia.* In order to do this, I put the platinum retort containing the salt to be sublimed on an iron plate in a gas-stove that I have described and illustrated on page 553 of my "New Researches on the Laws of Chemical Proportions," taking care to leave the *upper two-thirds* of the retort outside the stove, and to shield this part from the gases at the temperature of the volatilisation of sal-ammoniac, by means of a second iron plate.

Having ground the neck of the retort lid, as far as possible into a long tube, I passed a tube for the supply of dry ammonia, which was admitted through a cork at the other end of it, through it, as far as the entrance to the dome of the lid.

The air in the retort being entirely replaced by dry ammonia, I regulated the heat imparted to the gases by the combustion of coal-gas in the following manner, so as to sublime the sal-ammoniac slowly:—I put an open tube containing sal-ammoniac, with the upper end protruding from the stove, in the bottom of the retort, to act as a thermometer. When, by reason of the high temperature of the gas, I saw the sal-ammoniac crystallising *slowly* in rings on the upper part of the open tube, I kept the supply of coal-gas burning in the stove constant for five hours by means of a regulator. Five hours were actually required for slowly subliming about 150 grms. of sal-ammoniac, the quantity on which I was working.

I have gone into these minute details because I have been asked to do so by certain chemists who, having wished to obtain some sal-ammoniac sublimed in platinum, have failed to do so, though they followed the directions given on page 473 of my "New Researches on the Laws of Chemical Proportions."

Sal-ammoniac volatilised as I have just described, condenses in the same retort in the form of a *very thick, transparent, colourless, and elastic* ring, which becomes detached after cooling for some time, becoming entirely opaque. The domed top is filled with powdery sal-ammoniac, smelling strongly of ammonia, and rapidly taking up sodium from the air.

Sublimed chloride of ammonium gives no sodic characteristics to flames; but when kept under a bell-jar shielded from atmospheric dust, it slowly condenses sodium compounds on its surface, as all solids do under similar conditions.

Coming back to the treatment of chloride of potassium by chloride of ammonium.

To fuse chloride of potassium, I put in the bottom of a large platinum crucible, *quite free from iron,*[*] first of all a layer of alkaline chloride in powdered crystals, then a

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[*] A crucible made of pure platinum is deprived of the iron introduced into it by welding, by treating it, at a low red heat, with chloride of ammonium. This treatment is continued until one gets a *colourless* button of *melted* chloride on fusing a mixture of pure alkaline chloride and sal-ammoniac. So long as the platinum retains traces of iron, an alkaline chloride melted in it with sal-ammoniac forms a red or pink mass, and looses the ferric oxide when dissolved in water. Alkaline chlorides dissolve ferric oxide when melted, and loose it when cooled. It is only necessary to dissolve melted ferriferous chlorides in cold water to obtain, on filtering the solution and evaporating the liquid, a perfectly white saline mass, which one can melt in a pure platinum crucible with sal-ammoniac, and form, on solidification, an absolutely colourless button.

piece of sal-ammoniac, and finally I filled the crucible with melted chloride mixed with small pieces of sal-ammoniac.

After putting the lid on the crucible, I warmed it slowly to a dull red heat, then I kept it at least fifteen minutes at a *bright red heat*, until, on lifting the lid, the gas bubbles seen round the edge of a crucible containing an alkaline chloride melted with sal-ammoniac, had entirely disappeared. I quickly poured the chloride into a recently heated and cooled platinum dish. If the operation has been properly conducted—that is to say, if the chloride has been kept fused at a high temperature for a sufficient length of time—the button is *colourless, limpid, and transparent*, and contains no gas bubbles.

When I found bubbles present, a sign of the existence of sal-ammoniac or of the products of decomposition, *I re-melted the button* in a double crucible of pure platinum, and I then turned the melted chloride into a platinum dish.

The buttons, when cold, were broken in an agate mortar, and the pieces, the edges of which had become milky, were put into flasks with ground glass stoppers.

Since they were made from chlorates and perchlorates which left no trace of solid residue on volatilisation, I naturally dispensed with testing the chlorides afresh. The very great care that I took during the work to prevent siliceous and sodic atmospheric dust from falling into the salt is a sufficient guarantee for its purity.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1895.

Mr. A. G. **VERNON HARCOURT**, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. John Allan, 242, Moss Lane East, Manchester; Herbert Lister Bowman, 13, Sheffield Gardens, Kensington, W.: James Kerry Burbridge, Moor's Lea, Winchmore Hill; Frank Dixon, 73, King Edward Road, South Hackney, N.E.; Joseph Edward Morrison, Montreal; Harold Rostron, 70, Davenport Street, Bolton; Peter B. Scotland, 30, Stirling Street, Airdrie, N.B.; Aitken Migget Simpson, 4, Kitto Road, St. Catherine's Park, S.E.; Henry G. Smith, Technological Museum, Sydney, N.S.W.

Mr. **OTTO HEHNER** called the attention of the Society to what he regarded as unprofessional conduct on the part of a Fellow of the Society whose name appeared on the certificates of certain candidates who were to be ballotted for that evening.

Professor **ARMSTRONG** then moved, and Mr. **GROVES** seconded, that the Council be requested to consider this case. Professor **TILDEN** having spoken in support of the motion, it was put to the meeting and carried.

The following were duly elected Fellows of the Society:—George Percy Bailey, B.A., The Earl of Berkeley, Arthur Jenner Chapman, Wm. Chattaway, George Bertram Cockburn, B.A., Charles Crocker, Gurney Cuthbertson, William Dixon, Edward Henry Farr, Charles James Fauvel, Patrick Joseph D. Fielding, Jervis E. Foakes, Stanley Fox, James Gardner, Edward Graham, B.Sc., Edward Henry Grossmann, The Rev. Henry Arthur Hall, M.A., Edgar Septimus Hanes, C. E. Harrison, B.A., James Henderson, B.Sc., Thomas Hawkins, Percy Heriot, Frederick Arthur Hillard, B.A., Arthur Edward Holme, M.A. (Oxon.), Alfred James, Frederick Edward Johnson, William Oakes Kibble, Leonard P. Kinnicut, James McCreath, David James Morgan, William Henry Pennington, Martin Priest, W. T. B. Ridge, William Round, William Augustus Rugginz, Clarence Arthur Seyler, B.Sc., Mathew Smith, B.A., Frank R. Stephens, George Stone, W. J. Tibbals, John Williams, B.A., Thomas Rowland Wingfield, and Harold E. Wright.

Of the following papers those marked * were read —

*141. "*Researches on the Terpenes. VI. Products of the Oxidation of Camphene: Camphoic Acid and its Derivatives.*" By J. E. **MARSH** and J. A. **GARDNER**.

In this paper some of the oxidation products of camphene are described, among them being camphoic acid, $C_{10}H_{14}O_6$, as chief product, camphoric acid in small quantity, terephthalic acid, and succinic acid.

From camphoric acid were obtained:—Anhydrocamphoic acid, $C_{10}H_{14}O_5$; cis- and trans-camphopyric acids, $C_9H_{14}O_4$; camphopyric chloride, $C_9H_{12}Cl_2O_2$; chlorocamphopyric chloride, $C_9H_{11}Cl_3O_2$; chlorocamphopyric anhydride, $C_9H_{14}ClO_3$; camphopyranilic acid,—

$$C_9H_{13}O_3(NHC_6H_5);$$

and salts of camphoic and camphopyric acids. With camphopyric acid is compared camphoric acid in respect of their both existing as cis- and trans-isomers, and also as regards the acid chloride, chloroacid chloride, and chloroanhydride, producible from both camphoric and camphopyric acids.

The reduction of camphopyric acid to hexahydrometaxylene has also been accomplished, while the constitution of camphene is discussed from the general analogy of camphoric and camphopyric acids, from the probability of their both containing a hexamethylene nucleus, from the fact of the production of both acids from camphene and from the probability that neither camphoic acid nor camphopyric acid is producible from camphoric acid.

DISCUSSION.

Professor **ARMSTRONG** inquired whether Mr. Marsh could give any further information as to the isomeric bromocamphor described by him on a previous occasion, since he (Profesor Armstrong) had not been able to confirm Mr. Marsh's results.

If a molecular proportion of bromine be added to camphor heated on the water-bath, using 1 or 2 per cent in excess, so as to ensure the absence of camphor, an almost theoretical yield of bromocamphor (m. p. 76°) is obtained. If, to purify the product, it be dissolved in hot alcohol, the greater part of the bromocamphor at once crystallises out as the solution cools, and if the small amount of oily residue obtained from the mother-liquor—a mixture of mono- and dibromo-camphor—be digested with alcoholic potash, so as to reduce the dibromo-compound, this also is converted into well-crystallised bromocamphor.

According to Marsh (*Trans. Chem. Soc.*, 1890, 828), if camphor be brominated in presence of alcohol, almost half the product consists of an isomeric bromocamphor of ill-defined crystalline form and very low rotatory power. A product such as he describes can undoubtedly be obtained, but it is not difficult to separate bromocamphor from it, and its properties are certainly those of an impure material. It is desirable that this product should be more fully examined, and its nature definitely established, in view of the interest attaching to isomeric cis- and trans-modifications of camphor derivatives; the account given by Marsh is incomplete as it stands, and it is to be hoped that he will study further the action of bromine on camphor in presence of alcohol.

Mr. **MARSH**, in reply, said he had no doubt as to the existence of the second bromocamphor. He regarded the action of bromine on camphor as very considerably modified by the presence of alcohol, which, by reacting at once with the hydrobromic acid to form ethyl bromide, favoured the existence of the unstable isobromocamphor. The isobromocamphor has been obtained in crystals having a definite melting-point. Its specific rotation is more than 100° lower than that of the ordinary modification, while it is also lower than that of camphor itself. When distilled it is converted partially, without appreciable decomposition, into the ordinary modification, the rotatory power after one distillation being raised about 50°, whilst ordinary bromocamphor may be readily obtained from the distilled product by crystallisation from alcohol.

*142. "*New Derivatives from α-Dibromocamphor.*" By Martin O. Forster, Ph.D.

Early in this year a preliminary note was published in the *Proceedings* (p. 4), describing the behaviour of α-dibromocamphor towards nitric acid, an investigation undertaken at the suggestion of Professor Armstrong. It appears desirable to place on record the results which have since been obtained in this connection.

It has been already stated (*loc. cit.*) that a compound of the formula $C_{10}H_{12}Br_2O_2$ is produced when α-dibromocamphor is acted on by fuming nitric acid (*d.* 1·52), and that reduction with zinc dust and alcoholic ammonia converts this substance into a compound of the formula $C_{10}H_{13}BrO_2$. A fuller investigation has shown that the composition of these products is represented by the formulæ $C_{10}H_{14}Br_2O_2$ and $C_{10}H_{15}BrO_2$ respectively, which, in fact, correspond more closely to the analytical results already published than do the formulæ previously chosen.

The compounds $C_{10}H_{14}Br_2O_2$ and $C_{10}H_{15}BrO_2$ having given rise to numerous derivatives, it has been found necessary to adopt some system of nomenclature by means of which they may be designated, and the scheme which is now proposed has been selected because it aims at representing in the name of a derivative the class of compounds to which it belongs. It having been found that the initial compound $C_{10}H_{14}Br_2O_2$ has the properties of a lactone, this substance will be referred to as *dibromocampholid;* the product of its reduction, $C_{10}H_{15}BrO_2$, is an unsaturated (carboxylic) acid, and will be called *bromocamphorenic acid*, the termination "olid" being significant of lactones, whilst ethylenic linking is represented by the syllable "en."

Dibromocampholid, $C_{10}H_{14}Br_2O_2$, is obtained by the action of fuming nitric acid (*d.* 1·52) on α-dibromocamphor in quantity amounting to about 10 per cent of the material used; it crystallises in long, colourless, transparent needles, and melts at 152°. Alcoholic potash converts it into the *lactone*, $C_{10}H_{14}O_3$, which melts an 174°, and yields the *acid* $C_{10}H_{16}O_4$ on hydrolysis; the lactone is readily converted by bromine into the *bromolactone*, $C_{10}H_{13}BrO_3$, which crystallises from alcohol in lustrous silky needles, and melts at 196—197°.

Bromocamphorenic acid, $C_{10}H_{15}BrO_2$, is formed when an alcoholic solution of dibromocampholid is reduced with zinc dust and ammonia; it crystallises from alcohol in thin, lustrous, six-sided plates, and melts at 159°. The *barium* salt contains $2H_2O$, and the *zinc*, *copper*, and *silver* salts are also crystalline; the *methylic* salt is a fragrant oil, which boils at 255° under a pressure of 767·5 m.m. The unsaturated character of bromocamphorenic acid is indicated by its behaviour towards potassium permanganate, which is immediately decolourised by the solution in sodium carbonate, a dicarboxylic *acid* being produced having the formula $C_{10}H_{16}O_6$, and melting at 184°; a cold solution of bromine in chloroform is at once decolourised by the acid in the same medium, hydrogen bromide and dibromocampholid being formed.

Camphorenic acid, $C_{10}H_{16}O_2$, is obtained by reducing a boiling alkaline solution of bromocamphorenic acid with sodium amalgam; it crystallises from alcohol in colourless needles, and melts at 161°. The *sodium* salt crystallises from strongly alkaline solutions in silky needles; the *methylic* salt is a colourless oil, which boils at 215° under a pressure of 767·5 m.m., and has the odour of camphor. The *anhydride*, $C_{20}H_{30}O_3$, melts at 84—85°.

α-Bromocampholid, $C_{10}H_{15}BrO_2$, is obtained by the action of concentrated sulphuric acid on bromocamphorenic acid, and is isomeric with that substance; the production of an isomeric lactone under the influence of sulphuric acid, and the formation of a bromolactone on treatment with bromine, are features which characterise βγ-unsaturated acids. α-Bromocampholid crystallises from alcohol in lustrous plates, and melts at 92—93°; it is indifferent towards bromine, and is hydrolysed by a boiling aqueous solution of barium hydroxide.

β-Bromocampholid is isomeric with the foregoing substance, and is formed from camphorenic acid or the sodium salt and bromine; it crystallises from ether in transparent prisms, and melts at 62°. It is indifferent towards bromine, and when the alcoholic solution is reduced with zinc dust and ammonia, camphorenic acid is fnrmed.

Campholid, $C_{10}H_{16}O_2$, is obtained by dissolving camphorenic acid in concentrated sulphuric acid, the change being parallel with that attending the conversion of bromocamphorenic acid into α-bromocampholid; it is very readily soluble in most organic solvents, but separates from petroleum in minute white crystals, and melts at 176—177°. Campholid is very volatile, and sublimes slowly below 100°; it resembles camphor in appearance, and has the odour of that substance. It is indifferent towards bromine, but yields an acid, $C_{10}H_{18}O_3$, on hydrolysis, which crystallises from ethylic acetate in magnificent lustrous needles, melting at 179.

*143. "*Isomeric π-Bromo-α-nitro Camphors.*" By Arthur Lapworth, D.Sc., and F. Stanley Kipping, Ph.D., D.Sc.

It has already been shown by one of the authors (*Proc. Chem. Soc.*, cxlviii., 39) that π-dibromo-camphor is attacked by concentrated nitric acid, and that the product consists partly of a bromocamphoric acid and partly of an oil, which, by the action of alcoholic potash, yields a bromonitro-camphor.

It has now been found that if this oil be boiled with concentrated nitric acid until it is free from π-dibromocamphor; it subsequently solidifies to a crystalline cake, from which *bromonitro-camphor* can be easily isolated. (Found C=34·05; H=4·21; Br=44·98 per cent. Calc. C=33·80; H=3·67; Br=45·05 per cent).

This compound separates from cold light petroleum in the form of long flat needles, meling at 54°, and is insoluble in water, but soluble in most of the usual organic solvents. When boiled with alcoholic potash it loses 1 atom of bromine, and affords the potassium salt of the bromonitro-camphor previously described (*loc. cit.*). The further investigation of this bromonitro-camphor leads to the conclusion that it is polymorphous. The crystals from chloroform and petroleum melt sharply at 133—134°, and solidify on cooling to a crystalline mass, which fuses at 126°; this is also the melting-point of crystals obtained from alcoholic or dilute acetic acid solutions, whereas large pyramidal crystals deposited from a mixture of ethylic acetate and chloroform melt at 108°, immediately solidify, and melt once more at 126°. A 6 per cent solution gave $[\alpha]_D = +33{\cdot}04$.

Reduction of π-bromo-α-nitro-camphor with zinc dust and acetic yields an amido-compound with a strong ammoniacal odour, which is probably ordinary amido-camphor, as it contains no bromine, and agrees in properties with the compond described by Schiff (*Ber.*, xiii., 1404).

If, however, the bromonitro-camphor be carefully reduced with sodium amalgam in alkaline solution, it is converted into a new π-bromo-α-amido-camphor,—

$$C_{10}H_{14}BrONH_2,$$

the hydrochloride of which crystallises from water or acetone in colourlesss needles or plates. (Calculated for $C_{10}H_{14}BrONH_2{\cdot}HCl$, C=42·46; H=6·03; Br+Cl=40·81. Cl=12·56. Found, C=42·57; H=6·05; Br+Cl=40·36. Cl=12·70).

The oxalate is almost insoluble in water, and melts at 201°; the platinichloride forms silky yellow needles, melting with decomposition about 219°.

π-Bromo-α-nitro-camphor dissolves in hot hydrochloric acid, and the solution on cooling deposits crystals of a new compound, which is soluble in hot sodium carbonate solution, and separates from benzene in flat needles melting at 137°. This substance is an isomeric π-bromo-α-nitro-camphor. (Found, C=43·57; H=5·32. Calculated, C=43·47; H=5·07 per cent).

It differs from its isomeride inasmuch as it dissolves readily in hot water, crystallising from the solution in thin plates melting at 108°; it is also much less soluble in ethylic acetate and in benzene, and it yields a blue copper salt, that of its isomer being pink. Its specific rotation is also much greater, viz., $[\alpha]_D = +52·7$.

That these two π-bromo-α-nitro-camphor are structurally identical is probable from the fact that they both yield π-bromo-camphoric acid on oxidation with nitric acid; it is concluded, therefore, that the difference between these two substances is of the same nature as that subsisting between cis- and trans-modifications of cycloid derivatives.

*144. "*Derivatives of π-Bromocamphoric Acid.*" By F. Stanley Kipping, Ph.D., D.Sc.

π-Bromocamphoric acid, $C_{10}H_{15}BrO_4$, prepared by oxidising π-dibromo-camphor (*Proc. Chem. Soc.*, cxlviii., 33), is readily acted on by alkalis giving, according to the conditions of the experiment, a lactonic acid, $C_{10}H_{14}O_4$ (m. p. 164—165°), or π-hydroxycamphoric acid, $C_{10}H_{16}O_5$ (*Proc.*, cli., 88).

The lactonic acid is the initial, and not the final, product of the action, as was at first supposed; when heated with excess of aqueous potash it is converted into a salt of the π-hydroxy acid. The hydroxy acid, treated with acetic chloride, yields an acetyl derivative of its anhydride; this substance crystallises from ethereal petroleum in prisms melting at 89—90°, and is dimorphous, another modification melting at 86—87°. When the hydroxy acid is distilled, it yields as principal product a lactonic acid, $C_{10}H_{14}O_4$ (m. p. about 226°, isomeric with the compound referred to above, and identical with that obtained by heating π-bromo-camphoric acid with quinoline (*loc. cit.*). The lactonic acid of lower melting-point is also converted on distillation into the isomeride of higher melting-point, whereas the latter, on fusion with potash, gives the π-hydroxy acid.

π-Hydroxycamphoric acid and the lactonic acid melting at 164—165° are readily oxidised by nitric acid, giving an acid of the composition $C_{10}H_{14}O_6$ (*loc. cit.*), but the lactonic acid of higher melting point is exceedingly stable, and seems not to be attacked by boiling nitric acid; on prolonged treatment with alkaline permanganate, however, either at ordinary temperatures or at 100°, it yields, amongst other products not yet investigated, a small quantity of a derivative of dihydroxycamphoric acid, $C_{10}H_{16}O_6$, namely, a hydroxylactonecarboxylic acid of the composition $C_{10}H_{14}O_5$. This substance crystallises from hot water, in which it is readily soluble, in long, slender needles, and from a mixture of moist ether and ethylic acetate in well-defined transparent prisms melting at about 265°; these crystals lose $1H_2O$, and become opaque when heated at 100°, so that the substance is probably a monohydroxylactonic acid of the composition $C_{10}H_{14}O_5+H_2O$, and not a dihydroxy compound. Its identity with the acid obtained from π-dibromocamphoric anhydride (see following note), and the fact that the lactone ring in the substance (m. p. 226°) from which it is derived is very stable, lead to the conclusion that it is the π-hydroxy group which has taken part in the lactone formation.

It seems probable, from the facts already established, that the π-bromine atom in π-bromocamphoric acid is a constituent of a $-CH_2Br$ group.

145. "*π-Dibromocamphoric Acid and its Derivatives.*" By F. Stanley Kipping, Ph.D., D.Sc.

The derivatives of π-bromocamphoric acid, which have been referred to in the preceding and in previous notes, are so stable that attempts to obtain from them simple oxidation products containing less than 10 atoms of carbon have so far been unsuccessful; as they also resist the action of bromine, or give with it ill-defined substances, experiments were made with the object of brominating π-bromocamphoric acid itself, in the hope of obtaining a dibromo-derivative which, on treatment with alkalis, would yield products more easily oxidisable than those prepared from the monobromo acid.

π-Dibromocamphoric anhydride, $C_{10}H_{12}Br_2O_3$, is obtained on treating dry π-bromocamphoric acid with bromine and amorphous phosphorus under the usual conditions; it crystallises from chloroform in large transparent plates, melts at about 210° without decomposing, and is readily soluble in warm chloroform, but very sparingly in cold ether, and insoluble in cold water and cold sodium carbonate solution.

π-Dibromocamphoric acid, $C_{10}H_{14}Br_2O_4$, is deposited in small plates when the anhydride is dissolved in hot concentrated nitric and the solution evaporated on the water-bath; it melts and decomposes at 210—211°, and is readily soluble in cold ether, but insoluble, or nearly so, both in chloroform and in hot water. It dissolves in dilute sodium carbonate solution with effervescence, and on acidifying the solution after heating for a few minutes π-bromocamphanic acid (see below) is precipitated. π-Dibromocamphoric acid is stable at 100°, but when heated at its melting-point, part is re-converted into the dibromo-anhydride and part is transformed into π-bromocamphanic acid with liberation of hydrogen bromide.

π-Bromocamphanic acid, $C_{10}H_{13}BrO_4$, is formed when the dibromo-anhydride is boiled for some hours with water and a little alcohol; it separates from cold dilute alcohol in fern-like crystals which contain water, but from hot water and from a mixture of chloroform and ethyl acetate anhydrous crystals are deposited; it melts at 176—177°, and is soluble in sodium carbonate solution with effervescence.

On prolonged boiling with water, or on heating with aqueous alkalis, π-dibromocamphoric acid is converted into an acid melting at about 265°, and identical with the oxidation product described in the preceding note.

146. "*w-Bromocamphoric Acid.* By F. Stanley Kipping, Ph.D., D Sc.

The fact that π-bromocamphoric acid is obtained directly on oxidising π-dibromocamphor, whereas the π-dibromocamphoric acid can be prepared from the corresponding anhydride (see preceding abstract), led the author to try and isolate the unknown bromocamphoric acid corresponding with Wreden's bromocamphoric anhydride: this was accomplished by hydrolysing the anhydride with concentrated nitric acid under suitable conditions, but the yield was comparatively small, most of the anhydride being recovered.

The bromocamphoric acid, which, it is proposed, should be distinguished from the isomeric π-acid by using the initial letter of Wreden's name (he having first prepared the anhydride), crystallises from a mixture of chloroform and ether in large transparent orthorhombic pyramids, having the composition $C_{10}H_{15}BrO_4$. (Found, C=42·9 H=5·4; theory, C=43·0, H=5·4 per cent). It dissolves freely in ether, but is almost insoluble in benzene and chloroform, and melts at 195—196°, charring slightly and effervescing; it is readily soluble in sodium carbonate solution, by which it is rapidly decomposed, yielding ordinary camphanic acid. When heated for a short time with acetic chloride the acid is re-converted into the anhydride from which it is derived.

Aschan (*Ber.*, xxvii., 2112, and xxviii.; Ref. 922) has recently isolated an acid, which he designates *l*-bromisocamphoric acid; this compound appears to be different from the acid which forms the subject of the present communication, but Aschan's original paper being at present inaccessible, this point cannot be finally settled.

The author also refers to a curious phenomenon observed in crystallising *w*-bromocamphoric anhydride from chloroform; in some cases the solution becomes highly supersaturated, and crystallisation ultimately takes place with almost explosive violence.

147. "*π-Chlorocamphoric Acid.*" By F. Stanley Kipping, Ph.D., D.Sc., and William J. Pope.

Optically inactive camphor sulphonic chloride (Kipping and Pope, *Trans.*, 1893, lxiii., 548) yields, on distillation, two products, namely, a crystalline inactive π-chlorocamphor and an oil (*Trans.*, 1895, lxvii., 371).

When the mixture of these two compounds is heated with nitric acid the oil is rapidly oxidised and passes into solution, but π-chlorocamphor, like π-dibromocamphor, is attacked and dissolved rather slowly.

On cooling the solution, crystals and an oil are deposited. The crystalline substance is π-chlorocamphoric acid, the oil being probably π-chloro-α-nitrocamphor, the formation of which, under the above conditions, would be analogous to that of $\pi\alpha$-dibromc-α-nitrocamphor from $\pi\alpha$-dibromocamphor (see preceding note by Lapworth and Kipping); other substances are present in the filtrate from nitric acid, but they have not yet been examined.

Inactive π-chlorocamphoric acid, $C_{10}H_{15}ClO_4$, resembles π-bromocamphoric acid very closely in ordinary properties. It is very sparingly soluble in hot water, from which it crystallises in small lustrous prisms, melting at about 195°. It is almost insoluble in chloroform, but dissolves freely in ether, methyl alcohol, and acetone.

This chloro-acid is doubtless structurally similar to π-bromocamphoric acid, but whereas the latter is a derivative of an optically active π-bromocamphor, the chloro-acid is derived from an inactive or racemic halogen derivative of camphor.

A chlorocamphoric anhydride has been recently described by Aschan (*Ber.*, xxviii., Ref. 922), but this substance is derived from an acid structurally as well as optically different from π-chlorocamphoric acid.

(To be continued).

NOTICES OF BOOKS.

Modern Copper Smelting. By Edward Dyer Peters, Jun. Seventh Edition, Re-written and greatly Enlarged. London and New York: The Scientific Publishing Company. 1895. 8vo., pp. 642.

When a work of this character has passed through the ordeal of seven editions, we may feel sure that it has given satisfaction to practical men.

The present edition takes due account of certain capital improvements in the metallurgy of copper, such as the introduction of automatic calcining furnace, the rapid development of the copper Bessemer process, the improvements in blast-furnaces and reverberatories, and "perhaps, above all, by the gradual dawning of the idea that although copper is worth fifteen times as much as iron it is not absolutely necessary to expend fifteen times as much money in handling and treating its ores."

This is a specimen of the dry humour which crops out here and there in this work. Thus we read that "it is easier to run a furnace on a novel plan with men who know nothing about it than with those who know too much."

On again speaking of cliques among workmen, Mr. Peters writes:—"A judicious mixture of nationalities will often prevent the deceptions and the attitude of passive resistance to all improvements which characterise a body of experienced workmen of any one nationality. A mixture of Irish and Cornish furnace-men with an American foreman usually works well, as the men all dislike and distrust each other so much that they find it impossible to combine against the common enemy."

The chapter on the distribution of the ores of copper loses much in value by its being confined to the North American deposits.

Automatic sampling is an improvement which must do away with some very unedifying disputes and recriminations, not merely in metallurgy, but in all the "heavy' chemical industries.

The Cornish fire assay of copper ores—a "Pferdemethods" as we have heard it called in Germany—is spoken of with too great leniency. A process which gives results short of the truth, not by a constant value, but by a proportion which fluctuates in different ores, ought no longer to be recognised. It is an error to say, as the author does in a foot-note, that "in England all analytical chemists are called assayers," though the exact connotation of the two terms has never been authoritatively defined. The electrolytic process for the determination of copper is very fully described and illustrated.

Under the cyanide assay, attention is called to the substances which interfere with the result. Arsenic and antimony rank as the most dangerous substances, as also zinc in proportions exceeding 4½ per cent. Ferric hydroxide, if present in quantity, occludes copper and introduces a serious error. Yet we once met with a chemist who considered he had effected an improvement in this process by omitting to filter off the precipitate of ferric hydroxide before titrating with cyanide.

In the improved cyanide method of A. H. Law, the copper is first precipitated from the solution of the ore by means of metallic aluminium, the deposit is re-dissolved by means of nitric acid. Silver, if any, is precipitated as a chloride and filtered off. For the subsequent titration care is taken that all the conditions shall be identical, such as the total volume of the solution, the proportion of ammonia used, and the working temperature.

The iodide process is very highly spoken of. After giving a table of results, the question is put—"Can the electrolytic method improve upon this?"

Pyritic smelting, in the strict sense of the term, *i.e.*, without the use of any carbonaceous fuel, is not, the author considers, sufficiently developed to warrant its introduction, except experimentally.

The Bessemer treatment of copper forms the subject of a very interesting chapter.

The most harmful substance which may be present in a matte is bismuth, as it adheres to copper most obstinately; and, according to the experiments of Hampe, renders it red-short even when occurring in such small proportions as 0·02 per cent.

The electrolytic refining of copper seems to have proved very successful in America, as shown by the enlargement of existing electrolytic works, and the establishment of new ones on the same principle.

A most valuable feature of the work must be recognised in the numerous and elaborate illustrations.

It is scarcely needful to add that the present edition of this book must be welcomed as a boon by all persons connected with the copper industry.

Treatise on Distillery. Distillers' Microbiology. Ferments and Fermentation. ("Traité de Distillerie. Microbiologie du Distillateur. Ferments et Fermentation"). By M. P. Guichard, Member of the Chemical Society of Paris. Paris: J. B. Baillière et Fils. 1896. Pp. 392, 16mo.

The study of fermentation is not merely a technological question. It was the earliest subject which led us to a clear conviction that chemical phenomena may involve and depend upon biological processes. This fact is of profound scientific importance. It shows us that the simpler sciences of Comte's hierarchy may and do require a knowledge of those more complex and less general.

But the work before us does more than it promises. It considers the animal and vegetable proteïc matters, the soluble and figured ferments, and the industrial analysis of fermented products.

The author gives a historic study of the process of fermentation. He traces the discovery of alcohol to Abucazi and Arnold, of Villanova, and quotes a recipe from

Ramon Lully for its production. He briefly traces the gradual development of the theory of fermentation and putrefaction down from those early experimentalists to the full light thrown upon the subject by Pasteur.

In the second part, M. Guichard considers the albumenoid substances in the widest sense of the word, the albumens, globulines, peptones, collagens, caseins, together with the genesis and transformation of the albumenoids in the organic economy.

The third section is devoted to the soluble ferments, diastases, zymoses or enzymes, and the theory of their action.

In the fourth section, we pass to the figured ferments—moulds, their aërobic and anaërobic life; yeasts, their origin, purification, and chemical composition. There is also an account of the reagents and pigments used in their microscopic examination. The microscope here figured and recommended is that of Vérick. For photographing the ferments we find the instruments of Dr. Roux (manufactured by Vérick) and of Nachet recommended and shown in the illustrations. As useful reagents, the author recommends a hot solution of glycerin, diluted sodium sulphate, and alum in very dilute solution, potassium acetate in an aqueous solution, the reagents of Barfoed, Fehling, Millon, and Ehrlich. The last-mentioned consists of 2 parts of potassium dichromate and 0·50 part copper sulphate in 100 parts water. The stains or dyes found most useful are described at some length.

In the fifth section we have the classification of fermentations, as the alcoholic, the bacterial (under which head are given some interesting facts as concerning the vital conditions of the Schizomycetes and the low temperatures which they are able to support), the acetic, the lactic, butyric, panary, gluconic, and mannitic.

The sixth section is occupied with the industrial analysis of the products of fermentation.

A selection of useful tables conclude the work.

M. Guichard's book may be regarded as useful, both from a practical and a theoretical point of view. Few chemists can now afford to overlook the multiform and far-reaching agency of fermentation.

CORRESPONDENCE.

ON THE
PLACE OF HELIUM IN THE CLASSIFICATION OF ELEMENTARY SUBSTANCES.

To the Editor of the Chemical News.

Sir,—In the Chemical News, vol. lxxii., p. 305, I notice that Dr. Gladstone maintains his wrong assertion "that the successive differences between the atomic weights of adjacent members of the metals in the first group in Mendeleeff's table showed that these differences increased as we go downwards," notwithstanding that the assertion was disproved by reference to this table, as well as to the one set forth in my former letter.

Judging from the remarkable statements now made by Dr. Gladstone, it would appear to be much more probable that he has forgotten the numbers he wrote on the blackboard of the Physical Society than that the official record of these numbers is incorrect.

As Dr. Gladstone, at the meeting of this Society, expressed doubt as to the elementary character of helium, he is hardly entitled to have an opinion on its place in any classification until he has first convinced himself on this point.

His observations on the relations of the atomic weights in the year 1853 have little in common with those set forth in my tables in the Chemical News of 1878 (vol. xxxviii.), which, as will be seen, anticipated everything of value that Dr. Gladstone advanced respecting the atomic weights in his Address to the Chemical Section of the British Association in 1883. No chemist knows this better than Dr. Gladstone himself.—I am, &c.,

H. Wilde.

December 21, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

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

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxi., No. 23, December 2, 1895.

Presence of Sodium in Aluminium produced by Electrolysis.—Henri Moissan. — This memoir will be inserted in full.

Origin of Argon and of Helium in the Gases given off by certain Sulphurous Springs.—L. Troost and L. Ouvrard.—(See p. 309).

Studies in Molecular Physics.—Ch. V. Zenger.—The author announces that he has found a simple relation between the density and the specific heat of the elements. This relation seems to him to throw a new light on the molecular actions which have governed the formation of the elements. Perhaps by imitating the characteristic conditions of the most remote geological epochs we may succeed in transforming the physical and chemical properties of the elements themselves.

Relation between the Intensity of Light and the Chemical Decomposition which it produces. Experiment with Mixtures of Ferric Chloride and Oxalic Acid.—Georges Lemoine.—The decomposition occasioned by light in solutions of ferric chloride and oxalic acid may serve for measuring the intensity of the light although the reaction is exothermic, for the heat disengaged is rapidly dissipated in the ambient medium, and the chemical transformation takes a permanent course. We may conclude approximately that the chemical decomposition of the mixture of ferric chloride and oxalic acid is proportional to the luminous intensity.

Presence of Argon and Helium in a Source of Natural Nitrogen.—Ch. Moureu.—(See p. 310).

Experimental Determination of the Agglutinating Power of Coal.—Louis Campredon.—There is no correlation between the composition of a coal as established by analysis and its caking power.

On Chromium Amalgam and on some Properties of Metallic Chromium.—J. Férée.—The author obtains chromium-amalgam by the electrolytic method. The product obtained had the composition Hg_3Cr. On submitting this compound to a pressure of 200 kilos. per square centimetre between folds of filter-paper another amalgam was obtained of the constant composition of HgCr.

Synthesis of Complex Amides.—Albert Colson.—Not suitable for useful abridgment.

New Instances of Superposition of the Optical Effects of Asymmetric Carbons.—Ph. A. Guye and Ch. Goudret.—Not suitable for abstraction and not of sufficient importance for insertion *in extenso.*

Revue Universelle des Mines et de la Metallurgie. Series 3, Vol. xxxi., No. 2.

Desulphuration of Cast Metal by the Saniter Process.—Krewtzoff.—The ingredient used is chiefly calcium chloride. In samples obtained the proportion of sulphur before the addition of the calcium chloride was from 0·029 to 0·035. After the process it was reduced to 0·019 to 0·016.

Determination of Sulphur in Organic Substances. L. L. de Koninck and Ed. Nihoul.—The authors submit the specimen operated upon to combustion with a mixture which they call nitro-lime. At least 5 parts of quicklime are incorporated with 1 part of dry calcium nitrate. The 5 parts of quicklime, in minute fragments quite anhydrous and free from sulphate and silicate, are placed in a porcelain capsule and gradually sprinkled with 1 part of dry calcium nitrate dissolved in ½ part water, applying a moderate heat if needful to set the reaction in progress. The method of operation has a general resemblance to that used in the Varrentrap and Will process for determining nitrogen.

MISCELLANEOUS.

The East London Exhibition.—It is announced that in June next there will be held, in the People's Palace, a General Exhibition of the Trades, Industries, and Arts of East London, and of the work of the Polytechnics and Technical Institutes. It includes the following Sections:—Exhibits of manufacturing and trading firms, the work of individual craftsmen; exhibits by individual students and apprentices; exhibits by students, collectively and by institutions; women's work, and loan exhibits of works of art. The first Section comprises the following groups:—The building trades; the silver trades, goldsmiths, jewellers, &c.; printing and allied trades; leather trades; clothing trades; engineering and metal trades; food and cookery; furnishing and brush and basket trades; shipping and navigation; tobacco trades; glass and pottery trades; coach-makers, wheelwrights, and auxiliary trades; textile trades; horticulture; aëronautics; brewing, and manufacture of aërated waters; fuel furnaces, stoves, and fireplaces; india-rubber; photography; educational and physical training appliances; toys and games; bicycles and tricycles; coopering; musical instruments; chemical manufactures—a department in which we have still much to learn; fire-arms and explosives; and, lastly, taxidermy. This last item will, we fear, include much that is injurious, if not absolutely criminal, *i.e.*, the destruction of harmless and useful birds and insects at the bidding of fashion. Under Section II. we find scientific instrument making, a department in which we have, nationally speaking, no little room for improvement. Prizes will be awarded in the various groups for excellence of workmanship. We hope that the Exhibition may prove successful in every sense, and that it may revive the original object of the People's Palace.

MEETINGS FOR THE WEEK.

Tuesday, Dec. 31st. } Royal Institution, 3. (The Christmas Lec-
Thursday, Jan. 2nd. } tures). "Sound, Hearing, and Speech,"
Saturday, Jan. 4th. } by Prof. J. G. McKendrick, M.D., F.R.S.
Friday, 3rd.—Quekett Club, 8.
— Geologists' Association, 8.

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END OF VOLUME LXXII.

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