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PHOTOMETRIC METHOD FOR THE QUANTITATIVE DETERMINATION OF LIME AND SULPHURIC ACID.[1]

BY J. I. D. HINDS.

Received May 14, 1896.

THE want of a rapid method of determining with a close approximation the amount of lime and sulphuric acid in drinking water led me to the study of the opacity of fine white precipitates suspended in water. I precipitated in weak solutions lime with ammonium oxalate, and sulphuric acid with barium chloride, then measured the height of a column of the liquid containing the precipitate through which the flame of a common candle was just invisible. I expected only a rude approximation, but to my surprise, I found that between certain limits, an accuracy is attainable equal to that of the ordinary volumetric methods.

APPARATUS.

The only apparatus needed is a cylinder graduated from the bottom in centimeters and tenths. The cylinder should have a plain polished bottom, like Nessler cylinders, and should have a lip at the top. The one I use was made for me by Eimer and Amend. It is four cm. wide and twenty cm. high. The graduations runs to eighteen cm. This cylinder, however, is not absolutely necessary. A common beaker may be used and the depth of the liquid measured with a small ruler.

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[1] The manuscript of this article was sent similtaneously to the Chemical News and to this Journal. Owing to the absence from home of Professor Hinds, his proof was delayed too long to allow of publication of the article in the July issue.

cm. x.	xy.
5.85	0.0573
6.4	0.0570
6.9	0.0566
7.475	0.0568
8.05	0.0564
8.65	0.0570

and dilution of the though very slightly. lutions more dilute with

	cm.	cm. x.	xy.
[illegible]	6.1	6.075	0.0595
[illegible]	6.6	6.925	0.0589
[illegible]	7.3	7.275	0.0597
7.9	7.9	7.9	0.0592
8.4	8.4	8.45	0.0591
9.1	9.1	9.075	0.0598
9.7	9.7	9.675	0.0590
10.2	10.2	10.2	0.0591
10.8	10.8	10.8	0.0594

.... 0.0593

six of first series.......... 0.0587

.... 0.0590

oduct xy, that is, the number obtained ent. of sulphuric acid in the solution by through which the flame is just invisi- he curve, therefore, made by taking the nd the other as the ordinate is an hyperbola ptotes, of which the equation is

$$xy = 0.0590.$$

shown in the accompanying diagram. The entimeters and the ordinates are 0.01 per cent. to r,

he equation for y, we have

$$y = \frac{0.0590}{x}$$

lphuric acid in any solution, observe

cipitate the whole of the calcium. The solution was then poured into the photometric cylinder and the depth measured as in the case of sulphuric acid. Portions of ten or twenty cc. of water were successively added and the depth observed after each addition. The results are given in the following table. In column 1 is the number of the solution; column 2 shows the per cent. of calcium carbonate; columns 3, 4, 5, 6, and 7 contain the measured depths of the liquid at which the flame became invisible; column 8 contains the means of these depths, and column 9 the product of these means by the per cents. in column 2, represented as before by xy. The three determinations in the fifth series were made simply as a check. Many other independent determinations were made in order to ascertain whether there was a change of opacity, and whether the precipitation would be different in the weaker solutions. No material difference was found.

No.	Per cent. calcium carbonate.	cm.	cm.	cm.	cm.	cm.	x.	xy.
1.....	0.0333	2.1	2.3	2.3	2.4		2.250	0.0750
2.....	0.0250	2.8	2.9	2.9	2.9		2.875	0.0718
3.....	0.0100	3.5	3.6	3.5	3.5		3.525	0.0705
4.....	0.0167	4.1	4.2	4.1	4.1	4.2	4.14	0.0691
5.....	0.0143	4.7	4.8	4.7	4.7		4.725	0.0676
6.....	0.0125	5.3	5.5	5.3	5.3		5.35	0.0669
7.....	0.0111	6.0	6.1	5.9	6.0		6.0	0.0666
8.....	0.0100	6.6	6.8	6.6	6.7		6.675	0.0668
9.....	0.0091	7.3	7.4	7.3	7.4	7.4	7.36	0.0670
10.....	0.0083	8.0	8.0	8.0	8.1		8.03	0.0666
11.....	0.0077	8.8	8.6	8.6	8.8		8.7	0.0670
12.....	0.0071	9.5	9.3	9.3	9.5		9.4	0.0667
13.....	0.0067	10.2	0.9	9.9	10.1	9.9	10.0	0.0670

Examining the values of xy, we find that they are not constant. They diminish rapidly at first, then more slowly. The equation is, therefore, not so simple as in the case of sulphuric acid. It appears, however, to be an hyperbola, and we may assume that its equation has the form

$$xy + by = a,$$

in which b and a are constants whose values are to be determined. Substituting the values of x and y from the above table, we obtain thirteen observation equations. The values of a and b are then found according to the method of least squares by forming and solving the two sets of normal equations. The first set will be the same as the observation equations; the second set is obtained by multiplying each equation by its cofficient of b. These equations are as follows:

$$\begin{array}{ll}
0.0750 + 0.0333\,b = a & 0.002500 + 0.001111\,b = 0.0333\,a \\
0.0718 + 0.0250\,b = a & 0.001795 + 0.000625\,b = 0.0250\,a \\
0.0705 + 0.0200\,b = a & 0.001410 + 0.000400\,b = 0.0200\,a \\
0.0691 + 0.0167\,b = a & 0.001151 + 0.000271\,b = 0.0167\,a \\
0.0676 + 0.0143\,b = a & 0.000967 + 0.000204\,b = 0.0143\,a \\
0.0669 + 0.0125\,b = a & 0.000836 + 0.000156\,b = 0.0125\,a \\
0.0666 + 0.0111\,b = a & 0.000740 + 0.000124\,b = 0.0111\,a \\
0.0668 + 0.0100\,b = a & 0.000668 + 0.000100\,b = 0.0100\,a \\
0.0670 + 0.0091\,b = a & 0.000610 + 0.000083\,b = 0.0091\,a \\
0.0666 + 0.0083\,b = a & 0.000553 + 0.000069\,b = 0.0083\,a \\
0.0670 + 0.0077\,b = a & 0.000516 + 0.000059\,b = 0.0077\,a \\
0.0667 + 0.0071\,b = a & 0.000474 + 0.000050\,b = 0.0071\,a \\
0.0670 + 0.0067\,b = a & 0.000449 + 0.000045\,b = 0.0067\,a
\end{array}$$

Adding the equations together, we have

$$0.8886 + 0.1818b = 13a. \qquad 0.012668 + 0.003304b = 0.1818a.$$

Dividing by the coefficient of a and eliminating, we have

$$a = 0.0642 \qquad b = -0.3$$

The required equation is therefore

$$xy - 0.3\,b = 0.0642,$$

or, solving for y

$$y = \frac{0.0642}{x - 0.3}.$$

For the per cent of CaO the equation is

$$y = \frac{0.0360}{x - 0.3}.$$

This is the equation of an hyperbola referred to one of its asymptotes as the axis of x and to an axis of y three-tenths cm. to the left of the other asymptote. The abscissas are centimeters and the ordinates are 0.01 per cent. to the cm. The curves are shown in the accompanying diagram.

As an example, let us suppose that the observed depth is four and seven-tenths cm. Subtract 0.3 and divide 0.0642 by the

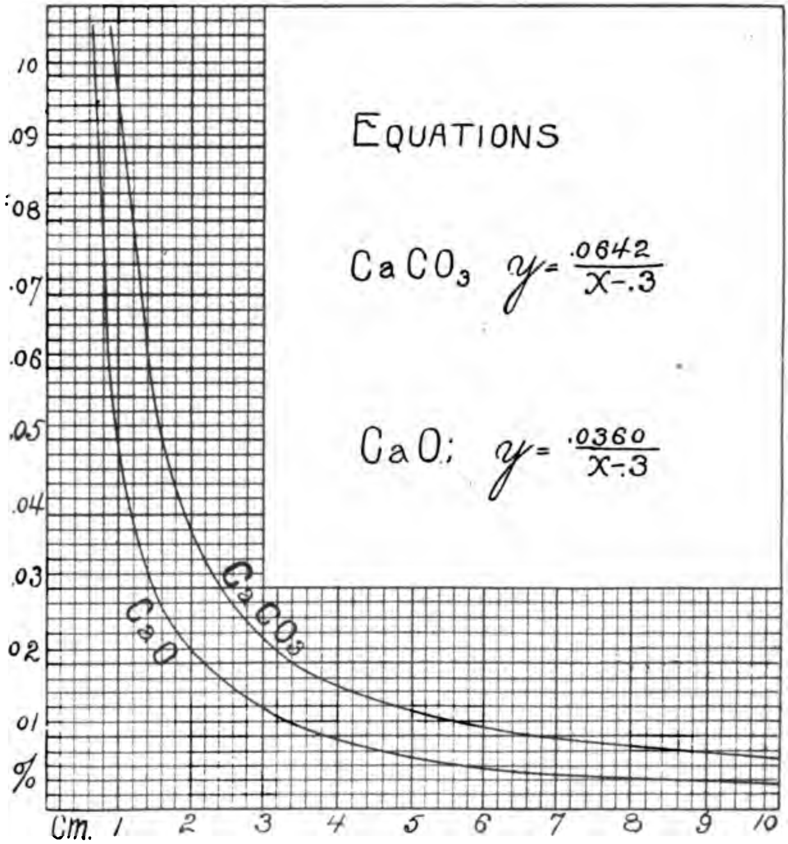

Diagram 2.

remainder. The quotient 0.0146 is the per cent. of calcium carbonate. Dividing this by 1000 we have 14.6 parts to the 100,000.

PROBABLE ERROR.

To determine the probable error of an observation we may compare as before the numbers found by observation with those computed from the equation, as follows:

x.	Strength used.	Strength computed.	v.	v^2.
2.9	0.0250	0.0247	0.0003	0.00000009
3.5	0.0200	0.0201	0.0001	0.00000001
4.1	0.0167	0.0170	0.0003	0.00000009

x.	Strength. used.	Strength. computed.	v.	v^2.
4.7	0.0143	0.0146	0.0003	0.00000009
5.35	0.0125	0.0127	0.0002	0.00000004
6.0	0.0111	0.0112	0.0001	0.00000001
6.7	0.0100	0.0100	0.0000	0.00000000
7.4	0.0091	0.0091	0.0000	0.00000000
8.0	0.0083	0.0085	0.0002	0.00000004
8.7	0.0077	0.0077	0.0000	0.00000000
9.4	0.0071	0.0071	0.0000	0.00000000
10.0	0.0067	0.0066	0.0001	0.00000901
			Sum Σv^2	0.00000038

Using the same value for error as before, in which in this case n, the number of observations, is 12, and q, the number of constants in the equation is 2, we have

$$r = 0.6745\sqrt{\frac{0.00000038}{12-2}} = 0.00013 \text{ per cent.}$$

That is, the probable difference between an observed and computed strength of a solution is 0.00013 per cent., or thirteen parts in ten million.

SOURCES OF ERROR.

The principal sources of error in this method are two. In the first place a light of constant intensity should be used. It makes but little difference what the light is, so it is the same as that with which the constant in the equation is determined. I employed the flame of an ordinary candle as the most convenient. A brighter and steadier light would give better results. Any change of light will of course change the constants.

The second source of error is the personal equation. Each individual can determine this for himself. The error dependent upon the eye can be almost eliminated by using it in the usual way, that is with or without glasses.

Any one can obtain the constants for himself by making a few determination with solutions of known strength. The best strength to use is that between 0.01 and 0.03 per cent. Great care must be used in measuring. If ten cc. of a decinormal solution are taken, a difference of one drop in the measurement may make an error ten times as great as that involved in the method.

PRACTICAL APPLICATION.

I have so far used the method and tested it only in sanitary water analysis and in the analysis of urine. To the water analyst it will be of great value. It gives the lime and sulphuric acid with almost the accuracy of the gravimetric method. It is more accurate than the soap test and is but slightly affected by the presence of magnesium salts.

For determining the sulphuric acid in urine I have found it quite satisfactory. The urine has to be diluted with nine volumes of water and then the color does not sensibly affect the determination.

I see no reason why this method may not be successfully used with all fine white precipitates. It is not suitable for precipitates that settle rapidly or gather quickly into flakes. Whether colored precipitates may be determined in this way is still to be investigated.

I desire to acknowledge obligation to Professor A. H. Buchanan for assistance in determining the equations and probable errors.

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[CONTRIBUTIONS FROM JOHN HARRISON LABORATORY OF CHEMISTRY.
No. 12.]

THE SEPARATION OF TRIMETHYLAMINE FROM AMMONIA.

BY HERMANN FLECK.

Received May 8, 1896.

THE quantitative estimation of trimethylamine in presence of ammonia is, I believe not mentioned in the literature, although a number of publications have appeared in which the detection of trimethylamine, in presence of ammonia, by means of the different solubilities of their hydrochlorides in absolute alcohol, has been successfully carried out.

Dessaignes[1] prepared and analyzed with good results the platinum double salt of trimethylamine, by conducting the mixture of ammonia and trimethylamine vapors into hydrochloric acid, evaporating to dryness, extracting with absolute alcohol, precipitating with platinic chloride and recrystallizing the precipitate formed several times from hot water.

[1] *Ann. Chem.* (Liebig), 81, 106.

Wicke[1] adopts the same method, using, however, alcohol-ether extract.

Winkeles,[2] in using this method, further states that while ammonium chloride is soluble to some extent in absolute alcohol, it is rendered totally insoluble by the presence of salts of such bases as trimethylamine.

Eisenberg,[3] by a similar procedure, obtained the platinum double salt in crystals of great purity and perfection.

The success in each case is undoubtedly due to the fact that large quantities of hydrochlorides were used. Winkeles,[4] for example, employed the hydrochlorides obtained from twenty-six gallons of herring brine. Further the mixtures were very rich in trimethylamine.

This method applied to a substance containing a low percentage of the latter yielded results, which clearly show that trimethylamine hydrochloride does not render ammonium chloride insoluble in absolute alcohol, and further does not serve as a good means of qualitative, much less of quantitative, separation. A portion of the mixture containing trimethylamine and ammonia was saturated with hydrochloric acid, evaporated to dryness and extracted several times with portions of several times the volume of boiling absolute alcohol. The alcoholic extract evaporated to dryness gave eighteen per cent. of supposed trimethylamine hydrochloride. To identify the latter, the residue was taken up with alcohol and platinic chloride added. The precipitate formed was redissolved in boiling water and the different fractional crystallizations, consisting of octahedra, analyzed.

	Pt found.	Required for
First crystallization	43.6	$(NH_4Cl)_2PtCl_4$, 43.84
Last "	39.5	Corresponding to a mixture of $2\Big((NH_4Cl)_2PtCl_4\Big)+$ $3\Big(N(CH_3)_3.HCl\Big)_2PtCl_4$, which require 39.4 per cent. Pt.

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[1] *Ann. Chem.* (Liebig), 91, 121.

[2] *Ann. Chem.* (Liebig), 93, 321.

[3] *Ber. d. chem. Ges.*, *1880*, 1669.

[4] *Loc. cit.*

Intermediate crystallizations gave intermediate, gradually decreasing results, showing that the isomorphous forms of the two salts crystallized together.

Duvillier, Buisine[1] extract the mixed *sulphates* to prepare pure trimethylamine from the technical product. The suggestion led to the use of the following method which yielded satisfactory results.

The mixed hydrochlorides are repeatedly extracted with portions of a total of five or six times the volume of boiling absolute alcohol and the solvent distilled off in a three-quarter liter distilling bulb. An excess of caustic soda is added to the residue and the gases formed on boiling driven over into a large quantity of water. Litmus is added, followed by the exact quantity of dilute sulphuric acid required to neutralize. The liquid is evaporated to dryness and extracted with one liter cold absolute alcohol, in which trimethylamine sulphate dissolves, leaving ammonium sulphate undissolved. The alcohol is distilled off, the residue transferred to a weighed dish, dried and weighed. In this manner 32,910 grams of the carefully dried mixed chlorides gave two and five-tenths grams trimethylamine sulphate, corresponding to 2.21 grams hydrochloride, or 6.71 per cent.

That the extraction was complete is evident from the total absence of the fishy odor when the extracted residues are treated with alkali. That the extracted material is pure is shown by the following analyses of the octahedral crystals of the platinum double salt prepared from the trimethylamine sulphate :

	Per cent. Pt.	Required for $[N(CH_3)_3.HCl]_2.PtCl_4$. Per cent. Pt.
I. 0.0983 gram gave..................	36.92	....
II. 0.3017 " "	37.12	36.93

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[1] *Ann. Chem.*, (Liebig) (5) 23, 299.

ZIRCONIUM TETRAIODIDE.

By L. M. Dennis and A. E. Spencer.

Received June 9, 1896.

WITH the exception of the tetraiodide all of the normal halides of zirconium have been prepared and described, the fluoride, chloride, and bromide being white, crystalline, sublimable solids.

A few attempts to make the iodide are recorded in the journals, but in no case was the normal compound, zirconium tetraiodide, ZrI_4, obtained. Melliss[1] passed the vapor of iodine over a glowing mixture of zirconia and carbon; he also treated zirconium tetrabromide with potassium iodide, but in neither case did zirconium tetrachloride result. Hinsberg[2] added an aqueous solution of barium iodide to a solution of zirconium sulphate, filtered off the barium sulphate, and evaporated the filtrate over concentrated sulphuric acid. He obtained a compound of the formula $Zr_2I_2O_3$, or $ZrI(OH)_3$. He also passed the vapor of iodine over a heated mixture of zirconium dioxide and carbon and states that no reaction whatever took place. Bailey[3] states that "zirconium[4] is acted upon by chlorine and bromine, in which, on gentle heating, it undergoes vivid combustion, forming the tetrahaloid derivatives, and this is, indeed, a convenient method for obtaining these bodies. The iodide could not be obtained."

In the work here to be described, the authors first attempted to prepare zirconium tetraiodide by passing the vapor of iodine over heated zirconium. The zirconium first used was made by reducing zirconium dioxide with magnesium powder, the two substances being mixed in the proportion employed by Winkler[5] and demanded by the equation

$$ZrO_2 + 2Mg = Zr + 2MgO.$$

This mixture was heated in hydrogen in the usual manner and the resulting black powder was removed from the boat, thoroughly ground, and again heated in hydrogen to insure

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[1] *Ztschr. Chem.*, *1870*. 296: *Jsb.*, *1870*, 328.

[2] *Ann. Chem.* (Liebig), 239, 253.

[3] *Chem News.*, 60, 8.

[4] Prepared by the reduction of zirconia with magnesium powder.

[5] *Ber. d. chem. Ges.*, 23, 2664; 24, 888.

conplete reduction. To free it from magnesia, the product was treated with a saturated solution of ammonium chloride. During this treatment a gas of very disagreeable odor was evolved. It is doubtless similar to that observed by Winkler at this point. The powder was then warmed with dilute twelve per cent. hydrochloric acid and, after collecting it on a filter, it was washed with water containing hydrochloric acid, then with alcohol and ether, and finally was dried in a current of hydrogen. The analysis gave

	Per cent
Zirconium	80.670
Silicon	0.807
Magnesium	0.117
Hydrogen	0.362
Oxygen (diff.)	18.044
	100.000

These results agree quite closely with those obtained by Winkler,[1] and indicate that the product of the reduction is chiefly zirconium monoxide rather than zirconium.

Although the powder probably contained but very little free zirconium, it was nevertheless heated in hydrogen and vapor of iodine was passed over it. An examination of the product gave no satisfactory indications, however, that an iodide of zirconium had been formed.

Inasmuch as the failure to obtain union between the zirconium and iodine might reasonably be ascribed to absence of free zirconium in the above product, it seemed advisable, before attempting any modification of the iodine treatment, to prepare zirconium by some other method and especially by some procedure in which the presence of any appreciable amount of oxygen is avoided. Under the circumstances the method of Berzelius,[2] the reduction of potassium fluozirconate with metallic potassium, seemed the most promising and was therefore employed.

The potassium fluozirconate was prepared from zircon. The zircon was finely ground, sifted through bolting cloth, and digested with concentrated hydrochloric acid until the acid gave

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[1] *Ber. d. chem. Ges.*, 23, 2667.

[2] *Ann. der Phys.* (Pogg), 4, 117.

no reaction for iron. The powdered zircon, which was now almost perfectly white, was dried and mixed with four times its weight of sodium carbonate. The mixture was fused in an assay crucible furnace, allowed to cool, pulverized, and repeatedly extracted with water. The residue, consisting of zirconia and unattacked zircon together with some silica and ferric oxide, was heated with concentrated hydrochloric acid, evaporated to dryness, and heated in an air-bath to 120° to render the silica insoluble. The dried mass was treated with a little hydrochloric acid, water was added, and the silica and other insoluble matter was filtered off. The filtrate, now containing zirconium chloride and some ferric chloride, was largely diluted with water, and ammonium hydroxide was added until there was formed a slight but permanent precipitate which was then dissolved by adding as little hydrochloric acid as possible. Sulphur dioxide was then passed into the solution until the liquid smelled strongly of the gas. In many cases a precipitate of basic zirconium sulphite formed at once, but, as the compound seemed to be somewhat soluble in an excess of sulphurous acid, the solution was always boiled for from ten to fifteen minutes to insure complete precipitation. In the reaction free hydrochloric acid is formed both by the conversion of the zirconium chloride into the basic sulphite and by the reduction of the ferric chloride to the ferrous salt. As this acid would dissolve the zirconium sulphite, it was partially neutralized by the addition, from time to time, of a few drops of dilute ammonium hydroxide. The zirconium precipitate not being wholly free from iron, it was dissolved in hydrochloric acid and again precipitated with sulphur dioxide. The pure zirconium basic sulphite thus obtained was dissolved in hydrochloric acid and zirconium hydroxide was precipitated by adding ammonium hydroxide. The well-washed hydroxide was dissolved in hydrofluoric acid, potassium fluoride was added, and the resulting potassium fluozirconate was dissolved in hot water and recrystallized.

The potassium fluozirconate thus prepared was reduced with metallic sodium, the operation being carried out in a cast-iron crucible. The crucible is cylindrical in form with an internal diameter of two inches and depth of five inches. The wall and bottom are over one inch in thickness. At the top it has a flange seven inches in diameter and is provided with a cast-iron cover one inch in thickness, which can be firmly fastened to the flange by means of six one-half inch bolts.

In charging the crucible, sodium chloride, finely ground and thoroughly dried, was first put in to the depth of about an inch and a half, and this was then well pounded down with a wooden plunger to compact the salt and expel the enclosed air. On top of the salt were placed alternate layers of potassium fluozirconate, also thoroughly dried, and metallic sodium, these being pounded down as before. The remaining space in the crucible was then filled with sodium chloride and, after pounding this down, the top was bolted on and the crucible was heated for about three hours with three triple burners. This heat, however, was not sufficient to raise the crucible to redness.

The crucible was then allowed to cool and, upon opening it, the charge was found to be so compact that it had to be loosened with a chisel. On treating the mass with water the metallic zirconium, together with a small amount of the oxide which had formed, settled to the bottom while the sodium chloride and potassium and sodium fluorides dissolved.

The zirconium and zirconium oxide were separated by first floating off the lighter zirconium with water and then digesting it with dilute hydrochloric acid at 40° until all of the oxide had been dissolved. The resulting product was a black, amorphous powder which, after washing with water, alcohol, and then with ether, showed no trace of impurity before the spectroscope except a slight amount of sodium.

Vapor of iodine was passed over some of this zirconium heated to dull redness in a current of hydrogen, but with no better success than with the other sample. We then concluded to substitute hydriodic acid gas for the iodine. Considerable difficulty was encountered in finding a suitable method of preparing the gaseous hydriodic acid. That described by Merz and Holzmann[1] was finally found to answer admirably. It consists in passing dry hydrogen and vapor of iodine through a red hot tube filled

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[1] *Ber. d. chem. Ges.*, 22, 867.

with pumice stone and freeing the hydriodic acid gas from iodine by passing the gases through cotton.

In treating the zirconium with hydriodic acid gas the following apparatus was used.

Iodine was placed in a small tubulated flask connected on one side with an apparatus furnishing pure, dry hydrogen and on the other side with a long piece of combustion tubing. The half of this tube nearest the iodine flask was filled with pieces of pumice stone and rested in a combustion furnace. The other half, extending beyond the combustion furnace, was filled with cotton. The end of this tube was connected with another combustion tube resting in a second combustion furnace. The porcelain boat containing the zirconium was placed in this second tube.

The hydrogen was first passed through the whole apparatus for several hours and then the first furnace was lighted. When the pumice had become red hot the flask containing the iodine was gently heated. The tube containing the zirconium soon became filled with the hydriodic acid gas, whereupon the second furnace was lighted. As the temperature rose, a brownish-yellow substance collected in the cold end of the combustion tube, but as the heat became greater the color entirely disappeared and there remained an amorphous white sublimate. No further sublimate was formed until the tube had almost reached a bright red heat when there appeared just beyond the point where the tube was red hot a white crystalline sublimate, different in appearance from that which first formed. The gas escaping from the end of the tube contained hydriodic acid, hydrogen, some iodine, and a trace of iron, the last probably being present in traces in the zirconium and volatilizing as ferrous iodide. The tube was kept at a bright red heat for from three to four hours. The gas was then turned off and when the boat had cooled considerably the heating of the iodine flask was discontinued. The first furnace was then shut off and the whole apparatus was allowed to cool in the current of hydrogen.

The material in the boat had changed from a black to a grayish-white color, but a chemical examination showed that it contained very little iodine. The amorphous sublimate which first formed was found not to be zirconium iodide but to contain chiefly iron and iodine.

The crystalline sublimate which was formed only at a red heat was next analyzed. These crystals were found to be insoluble in water, nitric acid, hydrochloric acid, aqua regia, and carbon disulphide. They were decomposed and dissolved by concentrated sulphuric acid ; they were also decomposed, but not completely, by concentrated nitric acid, iodine being liberated and a white powder, insoluble in the nitric acid, remaining. This residue was soluble in concentrated sulphuric acid and from this solution ammonium hydroxide threw down a white gelatinous precipitate. Upon dissolving this precipitate in hydrochloric acid and dipping turmeric paper into the solution, the orange color characteristic of zirconium was obtained. The solution gave no reaction for iron.

The zirconium in the compound was quantitatively determined by expelling the iodine by heating a portion of the salt with a mixture of sulphuric, nitric, and nitrous acids, dissolving the residue in concentrated sulphuric acid, diluting with water, and precipitating the zirconium with ammonium hydroxide. The precipitate was washed, dried, and ignited, and the zirconium weighed as the dioxide.

The iodine was determined by fusing some of the compound with about five times its weight of a mixture of potassium and sodium carbonate. The mass was then treated with water, filtered, and after acidifying the filtrate with nitric acid the hydriodic acid was precipitated with silver nitrate and weighed as silver iodide.

The results were

	Calculated for ZrI_4.	Found.		
	Per cent.	Per cent.	Per cent.	Per cent.
Zirconium	15.15	15.17	15.00	15.37
Iodine	84.85	85.34	85.27	....

The crystals when examined under the microscope proved to be clear, colorless cubes which showed no double refraction.

When heated for some hours in hydrogen the zirconium tetraiodide becomes black and iodine and hydriodic acid are formed. Heated in the air the iodide melts and sublimes. A weighed amount was placed in a porcelain crucible, covered with water, and evaporated to dryness. No change in weight and scarcely any in color resulted after two such treatments. This behavior toward water is surprising, for from the published descriptions of zirconium tetrachloride and tetrabromide, it was to be expected that the iodide would prove to be a hygroscopic compound easily decomposed by water. It seems, however, to more nearly resemble the fluoride which Deville states to be a colorless crystalline substance volatile at a white heat and insoluble in water or acids.

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PHTHALIMID.[1]

BY J. A. MATHEWS.

Received June 9, 1896.

A NUMBER of years ago Prof. C. E. Colby and Mr. Dodge, of Columbia University were led to try the effect produced by heating together, under pressure, mixtures of (1) fatty acids and fatty nitrils; (2) fatty acids and aromatic nitrils; (3) fatty nitrils and aromatic acids; and (4) aromatic acids and aromatic nitrils. The reactions were carried on in sealed tubes. The score or more reactions that they tried were done at temperatures ranging from 235° to 280° C. As the result of their work they reached these conclusions regarding what is likely to take place, at least when monobasic acids and mononitrils are employed.[2]

1. Fatty nitrils and fatty acids give secondary amids.
2. Fatty nitrils and aromatic acids give fatty acids and aromatic nitrils.
3. Aromatic nitrils and fatty acids give mixed secondary amids.
4. Aromatic nitrils and aromatic acids gave secondary amids, except in one case when exceptionally high heat was used (280°) in which case the cyanide of the higher radicle was formed.

In regard to dibasic acids and dicyanides not so much has been done. Miller first tried reactions with succinic acid and ethylene cyanide.[3] He found that succinimid resulted from each of the following experiments:

[1] Read before the American Chemical Society. New York Section, June, 1896.

[2] *Am. Chem. J.*, 13, *1891*.

[3] This Journal, 16, 443, *1894*.

1. Ethylene cyanide and acetic acid heated in a sealed tube.
2. Acetonitril and succinic acid, and
3. Ethylene cyanide and succinic acid.

Some other acids in this series have been tried. Malonic acid was rather imperfectly tested. In every case the tubes exploded and malonimide was not obtained at all.

Seldner[1] reports parallel results to those obtained by Miller when he used glutaric acid and trimethylene cyanide. In the following trials which he made glutarimid resulted every time:

1. Glutaric acid (1 mol.) and acetonitril (2 mols.).
2. Glutaric nitril (1 mol.) and acetic acid (2 mols.).
3. Glutaric acid and glutaric nitril, equal molecules.

Until the writer, at Prof. Colby's suggestion, made the experiments hereinafter recorded no one, to my knowledge, had applied these methods to aromatic, dibasic acids. The results of the first experiments are very gratifying and I hope in the near future to try the reaction with other dibasic, aromatic acids.

Since no information regarding phthalic nitril could be obtained I was obliged to do without it. The experiments were therefore made with phthalic acid and propionitril.

Four sealed glass tubes each containing phthalic acid (1 mol.) and propionitril (2 mols.), plus about three drops of acetic anhydride were heated in an oven for various lengths of time and at different temperatures.

Tube I. The first tube was opened after ten hours heating at 180° C. The contents of the tube had a pungent acid odor and were treated with cold dilute potassium carbonate solution. A residue consisting of needle-like crystals remained. These were filtered off, washed with water, and dried. The crystals then had a melting point of 228° C. I immediately suspected from this melting point that phthalimid had been formed by the reaction

$$C_6H_4(COOH)_2 + C_2H_5CN = C_6H_4(CO)_2NH + C_2H_5COOH.$$

The yield of phthalimid in this experiment was about sixty per cent. of the theoretical.

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[1] *Am. Chem. J.*, 17, 1895.

Tube II. On heating the remaining three tubes higher No. 2 broke at about 215°.

Tube III. After further heating of eight hours at 200° to 215° C. the third tube was opened and the contents treated with potassium carbonate solution. The crystals remaining were not so light colored as those from Tube I, and were so different in appearance that it was thought some other reaction had taken place. The melting-point, however, was about the same as in the first case, *viz.*, 227°. Yield eighty-four per cent.

Tube IV. Exploded at 258° C.

Since the theoretical equation requires only one molecule of nitril to one of phthalic acid two more tubes were prepared, each containing equal molecules of phthalic acid and propionitril.

Tube V. After three and a half hours at 180°–200° C. the fifth tube was opened and treated with potassium carbonate solution as before. Residue crystalline; melting-point 228.5°, yield eighty-eight per cent.

Tube VI. Heated five and a half hours at 180°–200°, melting point of residue, insoluble in cold, dilute potassium carbonate solution, 228.3° C., yield 92.5 per cent.

The crystals of phthalimid were all more or less colored, the color being darkest in the case of the third tube which had been subjected to long, high heat. In no instance was any outward pressure noticed on opening the tubes.

Portions of the products were recrystallized from acetic acid, from alcohol, and from alcohol with the addition of animal charcoal to decolorize. The melting points of the recrystallized products were a little higher than before purification, *viz.*, 230°, 229.5° and 229.5°, respectively. These agree very closely with the point given in Beilstein.

Biedermann[1] gives the melting-point as 228° or 229° C.

Michael[2] gives the corrected melting-point as 233.5° C. The decolorized crystals from alcohol form beautiful long needles.

Notwithstanding the close agreement of the melting-points obtained with those given by the authorities, some other tests were made to show that the product was nothing else than

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[1] *Ber. d. chem. Ges.*, 10, 1166.

[2] *Ber. d. chem. Ges.*, 10, 579.

phthalimid. A portion of the crystals heated with potassium hydroxide went into solution with evolution of ammonia. Another portion of the crystals were covered with concentrated ammonia and allowed to stand for some time. They were soon converted into microscopic crystals of phthalamid

$$(=C_6H_4(CONH_2)_2).$$

These crystals were filtered off, washed, and dried. They melted at 217.5° (uncorrected) with an evolution of ammonia, which began at about 200°. The phthalamid was further proved by its insolubility in cold water, alcohol, and ether, and by boiling it with water it was decomposed, giving off ammonia and on cooling phthalimid, melting at 230° C., crystallized out.

The results of these tests show conclusively that the product is phthalimid and that when it is made by the action of equal molecules of acid and nitril the yield is large. The reaction works comparatively readily, and at a much lower temperature than was needed to affect the reactions recorded by Colby and Dodge. It is highly probable that with slight changes of conditions any one of a variety of nitrils would give the same result. I hope to report further experiments with phthalic acid and other dibasic aromatic acids at a later day.

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DETERMINATION OF SULPHURIC ACID.

BY N. J. LANE.

Received May 19, 1896.

SOME months ago, before hearing of the controversy between Dr. Lunge and Mr. Gladding, some experiments were made on this subject, the results of which sustain Mr. Gladding's case. The determinations were made on nearly normal sulphuric acid to establish its strength with the following results:

	Barium chloride added suddenly.	Barium chloride added by drops.
1. Sulphuric acid	50.03	49.23
2. " "	49.90	49.32
3. " "	50.14	....

And the average of several practically identical titrations on C. P. sodium carbonate gave sulphuric acid 49.33.

The above results were obtained with the greatest care, and every precaution used to insure accuracy. This, in my opinion, conclusively proves the accuracy of Mr. Gladding's statements.

NOTE ON THE SOLUBILITY OF BISMUTH SULPHIDE IN SODIUM SULPHIDE, WITH SPECIAL REFERENCE TO THE ESTIMATION OF SMALL AMOUNTS OF BISMUTH IN ANTI-FRICTION ALLOYS.

By Thomas B. Stillman.

Received June 16, 1896.

THE method of separation of lead, copper and bismuth from antimony, arsenic and tin by the use of sodium sulphide is quite general. This is dependent upon the usually accepted statement that the sulphides of bismuth, lead and copper are insoluble, and the sulphides of arsenic, antimony and tin are soluble in sodium sulphide. This process of separation is employed in the analysis of various alloys, especially of anti-friction alloys, containing lead, tin, antimony, etc.

An alloy, used for similar purposes, but containing, in addition to lead, copper, antimony and tin, a very small amount of bismuth, was recently submitted to me for analysis.

After complete solution of the alloy in hydrochloric acid with a few drops of nitric acid, the acid was neutralized with sodium hydroxide, sodium sulphide solution (1.06 sp. gr.) added and the heat applied for twenty minutes. The solution was filtered and the filtrate examined for the antimony and tin with satisfactory results.

The precipitate of insoluble sulphides remaining upon the filter was found to contain lead and copper, but no bismuth. This indicated that the small amount of bismuth which was present in the alloy had gone into solution in the sodium sulphide.

To prove this theory, I weighed 0.128 gram of pure bismuth nitrate, dissolved it in twenty-five cc. of water with a few drops of nitric acid, the clear solution neutralized with sodium hydroxide, seventy-five cc. solution of sodium sulphide added, and warmed to a temperature near boiling for twenty minutes. The solution was filtered from the bismuth sulphide, remaining insoluble in the sodium sulphide. The clear filtrate was rendered faintly acid with hydrochloric acid, when a brownish-black precipitate immediately formed. This precipitate was filtered, dissolved in hot nitric acid and evaporated to dryness and ignited in a weighed porcelain crucible. The residue obtained was 0.031 gram of bismuth trioxide, and strongly yellow in color. It was dissolved in a few drops of hydrochloric acid, and the three following confirmatory tests for bismuth were made :

1. A portion of the solution was poured into a large amount of water, forming immediately a white precipitate of bismuth oxychloride.

2. A portion was tested by Schneider's test, the most delicate test for bismuth, the reaction obtained being strong and characteristic.

3. A portion was diluted with water, not enough to cause precipitation, and the solution saturated with hydrogen sulphide. The precipitate formed was brownish-black in color.

These three tests are absolutely confirmative of the presence of bismuth, and also show the absence of the other metals. By thus using pure bismuth nitrate for this test, lead, copper, antimony and tin are not present.

If now an analyst should weigh twelve grams of an alloy, composed approximately of lead eighty per cent., antimony fifteen per cent., tin 4.75 per cent., and bismuth 0.25 per cent. ("magnolia metal,)" and sodium sulphide solution be used for the separation of the tin and antimony from the lead and bismuth, *all* of the bismuth present would pass into solution and escape determination by the analyst.

No analyst, however, would use as much as twelve grams of such an alloy for analysis, but rather one or two grams.

If one gram be taken and sodium sulphide used as above indicated, three per cent. of bismuth might be present and *all* of it pass into solution in the sodium sulphide instead of remaining as an insoluble sulphide with the lead sulphide.

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STEVENS INSTITUTE OF TECHNOLOGY.

ON THE ESTIMATION OF SULPHUR IN PYRITES.

BY G. LUNGE.

Received June 19, 1896.

IT has taken Mr. T. S. Gladding six months to reply to my last paper on the above subject. I will not take much more than six days from the date of receiving the May number of the Journal of before dispatching my final reply to that gentleman.

Mr. Gladding avoids any mention, and of course offers no refutation, of the charges I had brought against him, but he again puts me into a totally false light, by saying that I "attempt no further support of my position by chemical experiment." This suppresses the fact that I had referred to my more than sufficient experimental proof for Mr. Gladding's and his assistants' inability to handle my process, which has been in daily successful use by scores, if not hundreds, of chemists for a number of years past, and is that employed in Fresenius' own laboratory, as I hear from his son-in-law and laboratory chief, Dr. Hintz. Mr. Gladding now exacts a further reply from me, more especially on the strength of some new comparative tests of what he states to be the main point at issue, namely the necessity of a very slow addition of the barium chloride.

I am convinced that our readers are as tired of this dispute as I am, but as some of them might construe my silence into the admission that Mr. Gladding is right on this point, and might saddle themselves with a total unnecessary complication in their daily work, I will not shirk a further reply, although I think it unnecessary after having quoted already in March, 1895, eleven experiments by entirely independent chemists, refuting all Mr. Gladding's assertions.

In his former paper Mr. Gladding states that the error caused by the rapid addition of the barium chloride solution is from two-tenths to three-tenths per cent. of sulphur, and according to his last paper it is even one-half per cent. He appeals to independent chemists to settle this discrepancy between his statements and my own. I have taken this up in the following manner: I instructed one of my assistants, Mr. U. Wegeli, a skilled worker, but entirely ignorant of the above dispute, to make a series of very careful tests of a sample of pyrites, just arrived for analysis and belonging to an important commercial case. I enjoined him to give me absolutely unvarnished results (which in our laboratory it would not have been at all necessary to say), and I told him, as we must be quite sure of the matter, he must not merely employ all the ordinary precautions, but also try both the usual quick addition of the barium chloride and a process recently very much recommended, namely, the very slow addition of the precipitant; I did not express any opinion of my own upon that point, and left it entirely for him to find out what there was in the matter. I had just then to undertake a short journey, and on my return he handed to me the following results.

A. *Quick* addition (*i. e.*, pouring in the hot barium chloride solution in about ten portions, occupying about half a minute in all, and stirring the mixture all the time, as every chemist would do).

1. 39.83 2. 39.65 3. 39.65 per cent. sulphur.

B. *Slow* addition from a burette, one drop per second (exactly as described by Mr. Gladding).

4. 39.63 5. 39.69 6. 39.44 per cent.

This means: In No. 2 and 3 the quick addition has given *identical* results with the slow addition in No. 4 and 5. No. 1 shows a little more, No. 6 a little less. I have suppressed nothing, and I give these results as well, although they are evidently not as reliable as the other four, entirely concordant, results; but even if we admit the less reliable results in striking an average, we find a difference of only one-tenth per cent. between the quick (39.71) and the slow (39.59) process. Such a difference is evidently within the limits of ordinary experimental error.

ZURICH.

[This discussion closes with the present paper.—ED.]

BACTERIA IN MILK SUGAR.

BY ALBERT R. LEEDS.

Received June 6, 1896.

CERTAIN phases of bacteriological investigations command universal and profound popular interest, and any publication relating to the connection of a specific organism with a zymotic disease, elicits general attention and discussion. This intimate connection of bacteriology with questions of life and death, has led many to regard the study as the proper province of medical specialists, despite the first uses made of bacteriological methods by Pasteur and his followers and to neglect them as instruments of chemical research. But the morphology, the classification, the physiology, and the botany of the bacteria are in such a rudimentary and unsatisfactory condition that the most valuable methods of bacteriological investigation are still of a chemical nature. The preparation of the culture fluids, the application of the tests, and the isolation of the products are chemical operations, and the advances to be made in the near future are to be looked for mainly on the chemical side of the subject. For this reason the absence from the columns of this Journal of papers resting upon the bacteriological questions, has been a matter of surprise to the writer, and the important contributions which have been herein recently made by Dr. Schweinitz, Dorsett, Bennett, Pammel, and Mason, a source of congratulation. Their results foretell the rich harvest of the future when the complete quantitative value of the chemical actions involved are known, and the different views which they may be expected to inaugurate as to the nature of many bodies now grouped closely together, but which deport themselves very differently when bacteria are the reagents made use of.

It is for these reasons that the writer desires to put on record the slight observations which he has made during the course of ordinary chemical work. They spring out of some anomalous behavior of specimens of milk sugar, which were being examined for purity. All the samples of pulverized milk sugar coming from the drug stores, which he examined, proved to contain a ferment when their solutions were kept at the optimum temperature for a sufficient length of time. The lactic acid produced was isolated in the form of calcium lactate. This was not the case with some lactose crystallized in nodular masses of prismatic crystals which had been obtained originally from Kahlbaum, and had been standing for twenty-five years in a stoppered jar. It was sterile. With the exception of this specimen, all the others gave an abundant crop of bacteria when definite weights dissolved in sterilized water were submitted to ordinary gelatin-peptone culture. The maximum number obtained in this medium was 1400 colonies per gram of milk sugar. In studying these colonies I looked more particularly for the bacillus *acidi lactici* and the other ten or twelve species, which are at the present time classified as the specific milk bacteria, but without success. With a lactose-litmus gelatin solution a still larger number of colonies was obtained and possibly larger search in this medium, might have revealed the specific milk bacteria of lactic acid fermentation. But my immediate object had been attained, and the presence of bacteria as a common impurity in lactose, to be looked for and avoided by the chemist and the druggist, sufficiently demonstrated.

THE QUANTITATIVE DETERMINATION OF THE THREE HALOGENS, CHLORINE, BROMINE AND IODINE, IN MIXTURES OF THEIR BINARY COMPOUNDS.

BY A. A. BENNETT AND L. A. PLACEWAY.

Received June 2, 1896.

CHEMICAL literature contains many records of methods for the quantitative estimation of the halogen elements, and for any one of these elements in the absence of the others they are as satisfactory as may be required. There are also, it is true, many suggestions and several proposed methods for the separation and estimation of these elements when present together or when some two are found in the same mixture, although they are generally unsatisfactory for one reason or another. The methods for qualitative determinations as given by Hart and by Kebler, in the *Journal of Analytical Chemistry*, are thoroughly satisfactory. A very convenient qualitative method that is in use in this laboratory consists in first using chlorine water, or euchlor, (made from potassium chlorate and hydrochloric acid), which immediately determines the presence or absence of iodine and in its absence that of bromine. Carbon bisulphide is used as the final indicator. If iodine is present more chlorine water is added and the whole is heated until the iodine color is replaced by the light yellow color due to bromine. This point is easily discerned. If now one or more of these halogens are present a portion of the original solution is treated with concentrated nitric acid and boiled until both of these elements are removed. This solution is now tested for chlorine by the usual methods.

There are several methods for the quantitative estimation of the halogens by the formation of their silver salts, the further treatment depending on whether two or three of these elements are present. In all cases, however, much time is required for the analysis and great care in the manipulation of the precipitates. Sexton says, in his work on Quantitative Analysis, Third Edition, that there is no known method by which the two acids, hydrogen bromide and hydrogen chlorine can be completely separated. He recommends their precipitation as silver salts, the weighing of this product and the conversion of the bromide present into the chloride by passing chlorine gas over the fused mixtures. From the results the amount of each halogen is determined. Of course the general procedure could be used if an iodide were associated with the chloride but would not be applicable in case all three halogens were present.

Dr. Prescott, in the *Journal of Analytical Chemistry*, 3, gives an acceptable method for the estimation of bromine in the presence of chlorine and calls attention to several others that have been employed. Fresenius gives, on pages 592 to 600 in the Second American edition of his work on Qualitative Analysis, elaborate methods for determining these elements in all possible mixtures of the binary compounds of these elements. They are generally difficult of application and employ rare reagents. It may be said, in general, that all methods of indirect estimation of the halogens in mixtures of their binary compounds are troublesome, although some of the recent modifications of these utes time was used for each distillation, but less time was usually sufficient. In fact most of the halogens were driven over during the first few minutes of heating after boiling temperature was reached. In case very great accuracy is not required an estimation can be completed in a few minutes.

It is evident that in all cases there must be relatively large excess of reagents. When the distillations were complete the iodine set free in the receiver was titrated against decinormal sodium thiosulphate. The titration can be made in the receiver but it was found most convenient to pour the liquid into a six-inch evaporating dish before estimation.

The contents of the flask are now removed to a beaker and the excess of the permanganate reduced by ferrous sulphate, adding sulphuric acid enough to render the solution clear. The solution was slightly warmed to hasten the action. It was then cooled and made up to a definite volume and an aliquot part estimated by precipitation with silver nitrate. There was nothing to prevent the estimation of the chlorine by titration, but no determinations were made by that method.

The following tables give the results of the work:

	Potassium iodide taken.	Iodine in potassium iodide.	Iodine found.	Potassium bromide taken.	Bromine in potassium bromide.	Bromine found.	Potassium chloride taken.	Chlorine in potassium chloride.	Chlorine found.
1	0.986	0.0754	0.0745	0.198	0.1330	0.1329	0.994	0.4869	0.4829
2	0.493	0.0377	0.0374	0.198	0.1330	0.1299	0.994	0.4869	0.4859
3	0.493	0.0377	0.0377	0.099	0.0665	0.0658	1.988	0.9738	0.9699
4	0.493	0.0377	0.0376	0.099	0.0665	0.0662	0.994	0.4869	0.4870
5	0.493	0.0377	0.0378	0.099	0.0665	0.0659	0.994	0.4869	0.4858
6	0.493	0.0377	0.0375	0.0495	0.0332	0.0328	0.994	0.4869	0.4867
7	0.493	0.0377	0.0375	0.0495	0.0332	0.0331	0.994	0.4869	0.4857
8	1.972	0.1508	0.1499	0.099	0.0665	0.0664	1.988	0.9738	0.9679
9	1.972	0.1508	0.1484	0.099	0.0665	0.0659	0.497	0.243	0.241
10	0.493	0.0377	0.0375	0.0495	0.0332	0.0329	0.497	0.243	0.242

The tabular statement needs no particular explanation. The quantities represented are the amounts in grams in each case.

It may be well to note that this general method is applicable for rapid technical estimations of bromine or of iodine either by themselves or in case of mixtures of the same. Single analyses can be readily made in ten to fifteen minutes.

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ON THE INVERSION OF SUGAR BY SALTS. NO. 2.

BY J. H. LONG.

Received June 29, 1896.

IN a recent paper[1] I have shown that in their behavior with cane sugar solutions many so-called neutral salts closely resemble weak mineral acids. Salts of the heavy metals in general have the power of inverting sugar solutions, and in some cases very rapidly, especially at an elevated temperature. The same fact has been pointed out for certain salts by others, notably by Walker and Aston,[2] who determined the speed of inversion of four nitrates, comparing them with dilute nitric acid. This inversion is due to the hydrolysis of the salts in question, the hydrogen of the acids formed being in all cases, probably, the active catalytic agent.

In my former paper I gave some results obtained in a preliminary investigation on ferrous iodide with very strong sugar solutions, and in the present paper I shall give the results obtained with other salts, as well as more extended tests with the iodide.

METHOD.

In the experiments before reported I made very strong syrups containing usually fifty grams of sugar in 100 cc., and to these syrups before final dilution weighed amounts of the salts were added, the volume being brought up to 100 cc. with distilled water. In the following series of tests the amount of sugar present is much smaller, being in all cases fifty grams in 250 cc. of the finished solution. This solution is much stronger than is usually employed in inversion experiments, but with many of the salts dissolved weaker sugar solutions could not be well used. The ferrous salts, especially, require relatively large amounts of sugar to hold them in clear solution, and as many of the experiments given below were made on such salts, it was decided to employ the same weight of sugar in all cases. For each experiment, therefore, fifty grams of pure sugar was dissolved in water in a 250 cc. flask by aid of heat. The strong syrup was cooled and to it was added the salt in the powdered form or dissolved in a little water. After securing a complete

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[1] This Journal, 18, 120.

[2] *J. Chem. Soc.*, July, 1895.

solution in either way, it was diluted to the mark and shaken to mix thoroughly.

The syrup so made was poured into small tubes of thin glass for inversion. These tubes held about twenty cc. and were three-fourths filled. They were cleaned for use by boiling in hydrochloric acid and then in distilled water repeatedly. After having been employed for several series of tests it was found sufficient to soak them twenty-four hours in weak acid, and then in distilled water, rinsing thoroughly finally. After receiving the sugar solutions they were closed with perforated rubber stoppers holding each a short glass tube with capillary opening. The tubes were placed in a receptacle, which was finally immersed in the water of a thermostat holding over twenty liters. The receptacle for the tubes consists essentially of two copper disks, twenty-five cm. in diameter, soldered six cm. apart on a copper rod as an axis. The lower disk is furnished with fine perforations, and the upper one with larger openings to receive the tubes. The copper axis below the lower disk ends in a hardened point, resting in a socket, and is extended above to a length of fifteen cm., ending in a grooved pulley around which a belt passes. Power applied to this belt rotates the tube receptacle, which at the same time keeps the water of the thermostat in motion. The thermostat itself consists of a large copper oven covered with asbestos boards on five sides. The top has perforations for the temperature regulator, thermometer and rotating axis of the tube receptacle. A section of the top can be quickly removed to take out tubes, but at other times should be left closed to exclude light. The capillary tubes in the stoppers closing the inversion tubes project about two cm. above the water.

With the apparatus employed it was possible to maintain a constant high temperature with a little watching through ten hours. A temperature of 85° was held with variation of less than 0.1° in either direction. With many salts the rate of inversion is exceedingly slow at ordinary temperatures, in fact almost imperceptible. For convenience in working, therefore, it was found necessary to invert at a high temperature, and 85° was

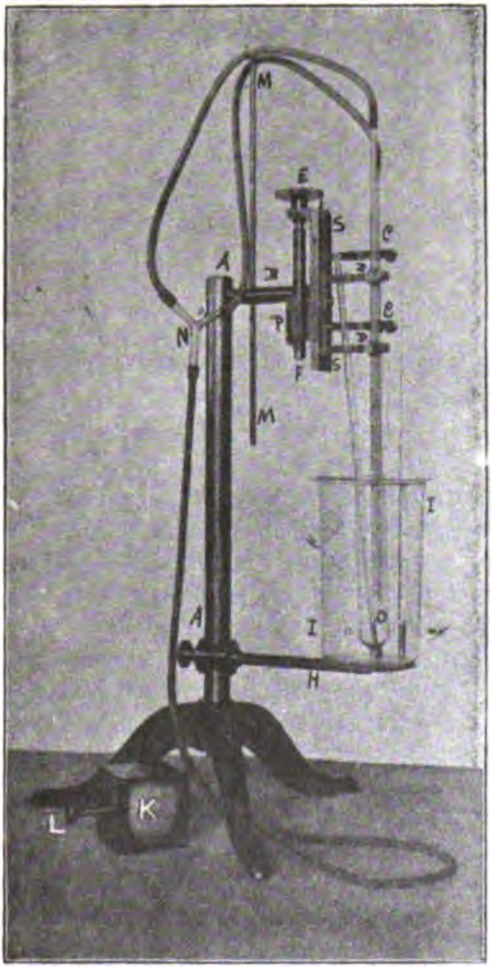

Fig. 1. Apparatus for Determining the Surface Tensions of Liquids. (*To Face p. 516.*)

chosen. In a few instances a slightly higher temperature was employed, but the results obtained are not included below.

The reaction between the sugar and salt is probably in most instances analogous to that between sugar and weak acids, and the rate of inversion may therefore be expressed by the same differential equation:

$$\frac{dx}{dt} = K(A-x).$$

The integration of this for t and $x = 0$, together, leads to the well known formula:

$$K = \frac{1}{t} \text{ nat. log. } \frac{A}{A-x},$$

where A represents the amount of sugar present at the beginning of the inversion, x that inverted at any time, t, of an observation, and K the "constant" or "coefficient" of inversion.

As the reaction is most easily followed by means of the polaristrobometer, A is conveniently measured by the total change in rotation which is observed between the beginning of the reaction and after complete inversion. x is measured by the change of rotation from the beginning up to the time, t, of any observation. For convenience common logarithms are employed in all the calculations below. As the sugar solutions were mixed with the inverting substances at a low temperature, the intervals, t, could be reckoned only from the time when the mixtures in the tubes had reached the constant temperature of the experiment. Preliminary tests were therefore made to determine several points of practical manipulation. The thermostat was first brought to a temperature of about 87°–88°, and the filled experimental tubes and their receptacle immersed in it. From this a fall of temperature resulted, because of the low temperature of the solution. In five or six minutes the constant temperature of 85° was reached, and by regulation of the gas flame this was maintained. In another set of experiments it was found that the solutions in the experimental tubes could be brought to a temperature of 85° from the room temperature in four to six minutes. It appeared, therefore, that ten minutes was amply sufficient time to allow, after introducing the tubes into the thermostat, before beginning the actual observations, and this was done in all cases in the experiments given below. In the case of bodies which invert but slowly there is little objection to the loss of this first ten minutes of the reaction, but in a few instances it was found to be a decided drawback, as will be seen below.

Usually 250 cc. of the solution was prepared for experiment, and this was filled into fifteen or sixteen tubes, and put into the thermostat. At the end of ten minutes a tube was withdrawn and cooled very quickly by immersion in cold water, or by holding it under a flowing hydrant. The contents were then poured into a polarization tube and polarized at the constant temperature of 20° in most cases. In a few tests made in warm weather a temperature of 25° was maintained in the dark room and in the water flowing around the observation tube. This first observation gives the initial rotation, and the time of removing the tube may be put as $t = 0$. Tubes were removed at different intervals following and treated in the same manner. The results of the polarizations were always very constant during the first few hours heating in the thermostat, as was found by removing and polarizing the contents of three tubes, but after five or six hours less regular results were found, and I adopted the plan of taking the mean result obtained by examining two or three tubes. With fifteen or sixteen tubes I made observations at eight or nine intervals.

After polarizing the liquids in the last tubes removed, the contents were mixed, returned to a tube and heated longer to obtain the end point of the reaction, that is, the point of complete inversion. The point found in this manner does not always agree with that calculated from the known weight of pure cane sugar in the original solution. Even with dilute acids the phenomenon of inversion is not as simple a thing as usually represented. As shown by Gubbe[1] and others, the specific rotation of invert sugar depends not only on the concentration, but on the time, temperature and acid used. Prolonged heating with salts produces in many cases, apparently, a slight

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[1] *Ber. d. chem. Ges.*, **18**, 2207.

decomposition of the levulose, from which the negative rotation of the invert sugar is found smaller than it should be theoretically. In a few instances, however, the negative rotation of the invert sugar was increased. From the experiments of Gubbe it may be calculated that fifty grams of cane sugar in 250 cc. would yield a solution after inversion, which in a 200 mm. tube should show a negative rotation of —8.6°. The rotation observed in my experiments was usually about —8.3°, but an accurate determination was not always possible, as some of the solutions became slightly colored before inversion was quite complete, and in other cases a negative rotation once observed seemed to grow slightly less on longer heating, making the exact end point somewhat uncertain. The discrepancies were not large in any case, however, and I decided to take —8.3° as the true end point for the 200 mm. tube, and —4.15° for the 100 mm. tube.

With some of the salts examined the velocity coefficient, K, is practically constant, with others it increases with the time, while in still other cases it decreases.

The sugar used in all the experiments was crystallized cut loaf of high degree of purity, and selected for the purpose. With fifty grams in 100 cc. it yields a solution of almost perfect clearness, which can be easily polarized in a 400 mm. tube. Weaker solutions yield, on inversion, results which agree perfectly with the theoretical requirement.

POTASSIUM ALUM.

Solutions of this salt invert very rapidly. A sample of pure alum was crystallized several times from distilled water to secure a product free from traces of uncombined sulphuric acid, sometimes present in the commercial article. This carefully purified salt was used in all the inversion tests. In the tables below, t refers to the time in minutes, and under α is given the observed angle of rotation in degrees and hundredths.

EXPERIMENT 1.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{64}$.

In 250 cc., fifty grams of sugar + 0.617 gram of alum.

$A = 33.03°$.

t.	a.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	24.73°	....	....	....
15	20.15	4.58°	0.06483	0.00432
30	16.16	8.57	0.13045	0.00434
60	9.75	14.98	0.26243	0.00437
90	4.85	19.88	0.39998	0.00444
120	1.25	23.48	0.53891	0.00449
150	—1.30	26.03	0.67581	0.00449
210	—4.88	29.61	0.98488	0.00468
270	—6.40	31.13	1.24016	0.00459
				0.00446

EXPERIMENT 2.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{32}$.

In 250 cc., fifty grams of sugar + 1.234 grams of alum.

$A = 32.37$.

t.	a.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	24.07°	....	....	....
15	17.83	6.24°	0.09300	0.00620
30	12.92	11.15	0.18339	0.00611
60	5.50	18.57	0.37026	0.00612
90	0.75	23.32	0.55349	0.00615
120	—2.48	26.55	0.74522	0.00621
150	—4.76	28.83	0.96114	0.00641
210	—7.00	31.07	1.39620	0.00661
270	—7.80	31.87	1.81117	0.00670
				0.00632

Experiment 3.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{16}$.

In 250 cc., fifty grams of sugar + 2.468 grams of alum.

$A = 31.25$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	22.95°	....	....	....
15	14.80	8.15°	0.13124	0.00875
30	8.79	14.16	0.26211	0.00873
60	1.07	21.88	0.52311	0.00872
90	—3.03	25.98	0.77304	0.00859
120	—5.64	28.59	1.06997	0.00891
180	—7.53	30.48	1.55533	0.00864
240	—8.15	31.10	2.31866	0.00966
				0.00886

Experiment 4.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{8}$.

In 250 cc., fifty grams of sugar + 4.936 grams of alum.

$A = 30.03$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	21.73°	....	....	....
15	11.23	10.50°	0.18686	0.01245
30	4.45	17.28	0.37205	0.01240
60	—2.87	24.60	0.74276	0.01238
90	—5.95	27.68	1.10649	0.01230
120	—7.34	29.07	1.49529	0.01244
180	—8.18	29.91	2.39838	0.01332
				0.01255

Experiment 5.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{4}$.

In 250 cc., fifty grams of sugar + 9.872 grams of alum.

$A = 29.19$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	20.89°	....	....	....
10	10.89	10.00°	0.18216	0.01822
25	2.10	18.79	0.44820	0.01793
50	—4.70	25.59	0.90893	0.01818
90	—7.73	28.62	1.70936	0.01899
150	—8.25	29.14	2.76626	0.01844
				0.01835

An attempt was made to invert with a half normal solution but at the temperature employed the rate was found to be too rapid for accurate observation.

With the first four solutions no difficulty was found in making accurate polarimetric observations in the 200 mm. tube. The last solution, however, became finally somewhat colored, and slightly turbid from precipitation of what appeared to be aluminum hydroxide. A portion, heated 180 minutes, became too turbid for direct reading and had to be examined in the 100 mm. tube after filtration. The rotation was found now to be —3.60°, corresponding to —7.20° for the 200 mm. tube, instead of —8.25° or —8.30°. From the slight concentration due to the filtration a still greater negative value instead of a lower one should be expected. We have here an illustration of the fact referred to above, *viz.*, that prolonged heating makes the end point determination somewhat uncertain at times.

It is interesting to note the relation existing between the concentrations of the solutions and their rates of inversion in the above examples. For comparison we can call the lowest concentration unity and arrange them as follows:

Conc		K
$\frac{N}{64}$	1	0.00446
$\frac{N}{32}$	2	0.00632
$\frac{N}{16}$	4	0.00886
$\frac{N}{8}$	8	0.01255
$\frac{N}{4}$	16	0.01835

Inspection of the table shows that the coefficient, K, increases rapidly with the concentration, but is not directly proportional to it. It is apparent that the numbers in the third column vary approximately as the square roots of those in the second, which is clearly shown in the next table.

Conc	K	$K_1 \times \sqrt{\text{Conc}}$
1	0.00446	0.00446
2	0.00632	0.00631
4	0.00886	0.00892
8	0.01255	0.01261
16	0.01835	0.01784

The regular results obtained from the aluminum salt are probably due in a measure to the inertness of the hydroxide toward sugar, as well as to the behavior of sulphuric acid in inversion. The bases of the other salts examined below form combinations with sugar more or less readily, not only with saccharose, but also with the products of inversion, so that the normal results of the reaction may be modified in a manner difficult to compute. The rather rapid rate of inversion in the above points to a relatively great degree of hydrolysis in the alum. Walker and Aston[1] found something similar in a half normal solution of the nitrate, studied at a temperature of 80°. From their polarizations a value of 0.0077 for K was found, and this was much in excess of the values found for other salts at the same time.

FERROUS SULPHATE.

A sample of the purest obtainable sulphate was recrystallized from water containing a trace of sulphuric acid, then dissolved in distilled water and precipitated by alcohol. The crystal meal secured was washed several times with alcohol and dried by fanning. The finished product was bright green and gave a nearly clear solution with pure water. It still held a trace of alcohol as disclosed by the odor. The experimental solutions were made by dissolving the sugar first and adding to this syrup the weighed sulphate meal. The mixtures were shaken to complete solution without application of heat, and then poured into the tubes for inversion. The solutions soon became turbid on warming and a minute amount of flocculent precipitate separated, making direct polarization impossible. The readings could be made therefore only after filtration, which was not without slight effect on the result. The total amount of separated hydroxide or basic salt was and remained through the test, minute.

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[1] *Loc. cit.*

EXPERIMENT 6.

$FeSO_4.7H_2O$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 17.38 grams of sulphate.

$A = 17.12$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	12.97	....	......	......
15	12.48	0.49	0.01261	0.00084
45	11.50	1.47	0.03899	0.00086
75	10.40	2.57	0.07064	0.00094
135	8.43	4.54	0.13382	0.00099
195	6.72	6.25	0.19727	0.00101
255	5.21	7.76	0.26222	0.00102
375	2.87	10.10	0.38716	0.00103
495	1.03	11.94	0.51917	0.00105
				0.00099

EXPERIMENT 7.

$FeSO_4.7H_2O$. N.

In 250 cc., fifty grams of sugar + 34.75 grams of sulphate.

$A = 17.10$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	12.95	....	......	......
15	12.45	0.50	0.01289	0.00086
45	11.26	1.69	0.04520	0.00100
75	10.08	2.87	0.07980	0.00106
135	8.07	4.88	0.14593	0.00108
195	6.30	6.65	0.21388	0.00110
255	4.70	8.25	0.28606	0.00112
375	2:25	10.70	0.42682	0.00114
495	0.15	12.80	0.59953	0.00121
				0.00107

Other tests were made with a second preparation of ferrous sulphate from which the alcohol had not been as completely removed. For a half normal solution the coefficient, 0.00094, was found, and for a normal solution the value, 0.00100, both results being but a trifle lower than those obtained from the pure products. It is possible that the differences may be due to the presence of the trace of alcohol. In any case it is evident that with solutions as strong as those used the larger amount of sulphate inverts but little more rapidly than the smaller.

AMMONIUM FERROUS SUPHATE.

But one experiment was made with this salt, a very nice crystallized preparation being used.

EXPERIMENT 8.

$(NH_4)_2Fe(SO_4)_2.6H_2O$. $\frac{N}{2}$.

In 500 cc., 100 grams of sugar + 49 grams of sulphate.

$$A = 17.08.$$

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	12.93	....	......	......
17	12.49	0.44	0.01134	0.00066
45	11.74	1.19	0.03137	0.00069
75	10.93	2.00	0.05409	0.00072
105	10.13	2.80	0.07776	0.00074
165	8.60	4.33	0.12698	0.00077
225	7.30	5.63	0.17368	0.00077
345	4.60	8.33	0.29048	0.00084
465	2.85	10.08	0.38739	0.00083
525	2.20	10.73	0.42972	0.00082
				0.00076

The coefficient is seen to be low, but nearly a constant. In this case, as in that of the ferrous sulphate, the mixture became slightly turbid on heating.

ZINC SULPHATE.

It is practically difficult to secure a good preparation of zinc sulphate crystallized without the addition of a trace of sulphuric acid. In absence of the acid crystallization is very slow. The preparation used below was made from a chemically pure commercial sample, by crystallizing with a trace of acid first and then from pure water, after heating the solution with pure zinc. The final crystallization to secure fifty grams required weeks for its completion. In my former paper attention was called to the fact that inversion with zinc sulphate is very slow, which is well shown below. The experiment was closed when the sugar was about half inverted, and as the coefficient is not regular, it is not possible to estimate accurately the mean rate for the whole period.

EXPERIMENT 9.

$ZnSO_4.7H_2O$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 17.94 grams of the sulphate.

$A = 17.25$.

t.	a.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	13.10	....	......	......
15	12.88	0.22	0.00558	0.00037
45	12.35	0.75	0.01935	0.00043
105	11.34	1.76	0.04674	0.00044
165	10.40	2.70	0.07393	0.00045
285	8.48	4.62	0.13539	0.00048
405	6.51	6.59	0.20903	0.00052
525	4.68	8.42	0.29083	0.00055

MANGANOUS SULPHATE.

After several attempts a salt was obtained crystallized from perfectly neutral solution. Some of the crystals were so irregular in outline that it was not possible to determine from inspection whether they contained four or five molecules of water. Determination of SO_4 in the product showed, however, that a very small amount only of the latter salt was present. In making the solutions I assumed for convenience that the compound had the formula $MnSO_4.4H_2O$, and weighed out accordingly.

As I pointed out in my former paper, a solution of manganous sulphate and sugar undergoes a peculiar decomposition when heated, in which a very fine dark substance is thrown out from solution. The amount of this is so small that I could not collect enough for tests, in the work done, but it is still sufficient to make the polarimeter readings very difficult. All solutions had to be filtered before examination, but even with this precaution the readings were often obscure.

EXPERIMENT 10.

$MnSO_4.4H_2O$, $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 13.94 grams of sulphate.

$A = 34.80$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	26.50°	....	......	......
45	26.33	0.17°	0.00213	0.000047
75	26.15	0.35	0.00439	0.000058
135	25.76	0.74	0.00934	0.000069
195	25.05	1.45	0.01848	0.000095
315	22.33	4.17	0.05543	0.000176
435	19.84	6.66	0.09226	0.000212
555	16.75	9.75	0.14277	0.000257

EXPERIMENT 11.

$MnSO_4.4H_2O$. N.

In 250 cc., fifty grams of sugar + 27.88 grams of sulphate.

$A = 34.75$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	26.45°	....	......	......
15	26.25	0.20°	0.00250	0.00017
45	26.00	0.45	0.00566	0.00013
75	25.75	0.70	0.00883	0.00012
135	24.90	1.55	0.01981	0.00015
195	23.00	3.45	0.04541	0.00023
315	18.20	8.25	0.11770	0.00037
435	14.45	12.00	0.18397	0.00042
555	9.50	16.95	0.29053	0.00052

EXPERIMENT 12.

$MnSO_4.4H_2O$. $2N$.

In 250 cc., fifty grams of sugar + 55.76 grams of sulphate.

$A = 34.42$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}.\log.\frac{A}{A-x}$.
0	26.12°	....	......	......
30	25.12	1.00	0.01280	0.00043
90	22.80	3.32	0.04405	0.00049
150	17.82	8.30	0.11984	0.00080
220	12.33	13.79	0.22231	0.00101
338	4.60	21.52	0.42622	0.00126
450	0.27	25.85	0.60383	0.00134
570	−3.80	29.92	0.88360	0.00155

EXPERIMENT 13.

$MnSO_4.4H_2O$. 3*N*.

In 250 cc., fifty grams of sugar + 83.64 grams of sulphate.

$$A = 34.00.$$

t.	α.	x.	$\log\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	25.70°	....	....	....
30	24.22	1.48°	0.01933	0.00064
90	18.76	6.94	0.09915	0.00110
150	11.50	14.20	0.23481	0.00156
220	4.75	20.95	0.41587	0.00189
338	—2.69	28.39	0.78252	0.00232
450	—6.25	31.96	1.22185	0.00272
570	—8.05	33.75	2.13354	0.00363

The rates of inversion cannot be directly compared in the above experiments because the latter were not carried to completion. In the first case over one-third of the sugar originally present was inverted, in the second case almost exactly one-half, in the third case about six-sevenths, while in the last case the inversion was very nearly complete. By plotting the results it is possible to determine approximately the rate of inversion when just one-half of the sugar has been inverted and this I have done. The results are given below, and show that the coefficients, *K*, are nearly proportional to the concentrations, these being referred to that of the half-normal solution as unity.

Conc.	K.
1	(0.00032)
2	0.00054
4	0.00109
6	0.00172

The first coefficient, 0.00032, is uncertain because it was found by a rather wide extrapolation, but between the others there is fair agreement.

MANGANOUS CHLORIDE.

The salt used was purified by several crystallizations from the best obtainable Schuchardt product.

EXPERIMENT 14.

$MnCl_2.4H_2O$. $\frac{N}{4}$.

In 250 cc., fifty grams of sugar + 6.18 grams of chloride.

$A = 35.00$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	26.70°	....	....	....
15	26.60	0.10°	0.00124	0.00009
45	26.30	0.40	0.00499	0.00011
75	26.00	0.70	0.00878	0.00012
135	25.25	1.45	0.01838	0.00014
255	22.66	4.04	0.05327	0.00021
375	18.75	7.95	0.11190	0.00030

The high initial rotation here is very extraordinary, corresponding to a specific rotation of 66.75°.

EXPERIMENT 15.

$MnCl_2.4H_2O$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 12.35 grams of chloride.

$A = 34.84$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	26.54°	....	....	....
15	26.45	0.09°	0.00113	0.00008
45	26.16	0.38	0.00476	0.00011
75	25.85	0.69	0.00869	0.00012
135	24.52	2.02	0.02594	0.00019
255	22.26	4.28	0.05693	0.00022
375	17.15	9.39	0.13639	0.00036
495	13.00	13.54	0.21370	0.00043
555	11.52	15.02	0.24498	0.00044

EXPERIMENT 16.

$MnCl_2.4H_2O$. N.

In 250 cc., fifty grams of sugar + 24.70 grams of chloride.

$A = 34.63$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	26.33°	....	....	....
15	26.12	0.21°	0.00264	0.00018
30	25.86	0.47	0.00593	0.00020
60	25.15	1.18	0.01505	0.00025
120	23.05	3.28	0.04321	0.00036
180	20.07	6.26	0.08659	9.00048
300	15.60	10.73	0.16105	0.00054

EXPERIMENT 17.

$MnCl_2.4H_2O$. 2*N*.

In 250 cc., fifty grams of sugar + 49.40 grams of chloride.

$$A = 34.18.$$

$t.$	$\alpha.$	$x.$	$\log. \frac{A}{A-x}.$	$\frac{1}{t} \log. \frac{A}{A-x}.$
0	25.88°	....	....	....
15	25.38	0.50°	0.00640	0.00043
45	23.91	1.97	0.02578	0.00057
75	22.21	3.67	0.04933	0.00065
135	18.25	7.63	0.10971	0.00081
195	14.80	11.08	0.17016	0.00087
345	5.25	20.63	0.40183	0.00116

No very plain relation can be found connecting these rates of inversion. The coefficients corresponding to the time of completion of one-third of the inversion are here given.

Conc.	*K*.
1	(0.00038)
2	0.00041
4	0.00055
8	0.00088

The first coefficient had to be estimated and is uncertain.

FERROUS CHLORIDE.

Considerable difficulty was experienced in preparing a solution of ferrous chloride devoid of traces of free acid. A weighed excess of pure iron wire was covered with water in a small flask and then the calculated volume of titrated hydrochloric acid was added in amount just sufficient to produce the solution of required strength. The mixture was gently warmed and allowed to stand a short time. Warming was repeated at intervals through several hours, until the liberation of hydrogen became very feeble. The solution so obtained stood five days in the presence of the excess of iron, being boiled twice in the interval, and was then filtered cold into the sugar solution, which was made up to the proper volume with fresh distilled water.

The actual strength of solutions made in this manner was determined by titration later. The two following were almost exactly normal and half-normal.

Both solutions became turbid on heating and had to be filtered before polarization for the first tests. After the lapse of about two hours the cloudiness disappeared and the solutions then taken from the thermostat were clear enough for direct polarization.

EXPERIMENT 18.

$FeCl_2$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 7.925 grams of chloride.

$A = 16.18$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	12.03°	....	....	....
15	9.47	2.56°	0.07507	0.00500
45	7.44	4.59	0.14517	0.00322
105	5.00	7.03	0.24783	0.00236
165	3.83	8.20	0.30725	0.00186
285	1.90	10.13	0.42749	0.00150
405	—0.50	12.53	0.64696	0.00160
525	—2.01	14.04	0.87884	0.00167

EXPERIMENT 19.

$FeCl_2$. N.

In 250 cc., fifty grams of sugar + 15.85 grams of chloride.

$A = 15.71$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	11.56°	....	....	....
15	9.40	2.16°	0.06424	0.00428
45	6.88	4.68	0.15360	0.00341
105	4.75	6.81	0.24679	0.00235
165	3.56	8.00	0.30913	0.00188
285	1.15	10.41	0.47190	0.00165
405	—1.42	12.98	0.76002	0.00187
525	—3.25	14.81	1.24194	0.00236

These results are very surprising, inasmuch as they show but little difference between the rates for the two concentrations. In both instances the rates rapidly decrease from the beginning and after the sugar has been about half inverted they increase a little. I give next some results from solutions which had not been boiled so thoroughly, and which may have held a little free acid.

EXPERIMENT 20.

$FeCl_2$. 0.52N.

In 250 cc., fifty grams of sugar + 8.242 grams of chloride.

$$A = 34.00.$$

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	25.70°	....	....	....
15	20.00	5.70°	0.07969	0.00531
45	12.80	12.90	0.20720	0.00460
75	9.00	16.70	0.29343	0.00391
105	6.19	19.51	0.37041	0.00353
165	2.42	23.28	0.50129	0.00304
285	—1.95	27.65	0.72771	0.00256
345	—3.96	29.66	0.89399	0.00258
405	—5.30	31.00	1.05436	0.00260

EXPERIMENT 21.

$FeCl_2$. 0.98N.

In 250 cc., fifty grams of sugar + 15.53 grams of chloride.

$$A = 33.60.$$

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	25.30°	....	....	....
15	19.84	5.46°	0.07702	0.00513
45	14.20	11.10	0.17416	0.00387
75	11.80	13.50	0.22314	0.00297
105	9.88	15.42	0.26675	0.00254
165	7.65	17.65	0.32358	0.00196
285	1.45	23.85	0.53734	0.00188
345	—1.50	26.80	0.69383	0.00201

The effect of free acid is not apparent. Six other experiments were made with normal and half-normal ferrous chloride solutions, the results of which were very similar to those above. In all cases the constant was found to increase before the completion of the inversion.

The constant for 0.001 N hydrochloric acid was determined for comparison at the same temperature, $t = 85°$, and with the same amount of sugar. It was found

$$K = 0.0051.$$

FERROUS BROMIDE.

Solutions of this salt were made by adding the proper amount of bromine to an excess of iron and water. A reaction soon begins which is hastened by heat. Finally the solution is thoroughly boiled, which eliminates all free bromine and leaves the iron in the ferrous condition. It is then filtered into the cold sugar solution and is ready for use. A solution so made is practically neutral.

EXPERIMENT 22.

$FeBr_2$. 0.54 *N*.

In 250 cc., fifty grams of sugar + 14.58 grams of bromide.

$A = 31.43$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	23.13°	...	....	....
15	16.76	6.37°	0.09836	0.00655
45	9.76	13.37	0.24062	0.00534
75	6.07	17.06	0.33988	0.00453
105	4.00	19.13	0.40743	0.00388
165	0.68	22.45	0.54406	0.00329
285	−4.03	27.16	0.86691	0.00304
345	−5.60	28.73	1.06598	0.00309

EXPERIMENT 23.

$FeBr_2$. 1.04 *N*.

In 250 cc., fifty grams of sugar + 28.08 grams of bromide.

$A = 29.50$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	21.20°	....	....	....
15	13.60	7.60°	0.12938	0.00862
45	6.22	14.98	0.30785	0.00684
75	2.90	18.30	0.42060	0.00561
105	0.75	20.45	0.51317	0.00489
165	−2.70	23.90	0.72163	0.00437
285	−6.35	27.55	1.17979	0.00414
345	−7.50	28.70	1.56673	0.00454

The normal solutions here invert but little faster than the half-normal. The rates in both cases diminish rapidly from the start, but after the middle of the inversion become nearly constant, as was observed with the ferrous chloride. The first three of the solutions taken from the thermostat had to be filtered before polarizing.

FERROUS IODIDE.

A half-normal solution was made by mixing 15.87 grams of iodine with an excess of iron and water, in the usual manner. On complete disappearance of the iodine the solution was boiled and filtered into a cold sugar solution. Water was finally added to make the volume up to 250 cc. The amount of sugar present is not sufficient to prevent some decomposition on heating, but, as in the other cases referred to, the turbidity at first noticed disappeared after longer warming in the thermostat. The first polarizations were made after filtering, and those later were made directly.

EXPERIMENT 24.

FeI_2. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 19.37 grams of iodide.

$A = 32.03$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	23.73°	....	....	....
15	17.45	6.28°	0.09478	0.00632
30	13.57	10.16	0.16571	0.00552
45	11.62	12.11	0.20627	0.00458
60	9.73	14.00	0.24956	0.00416
90	7.50	16.23	0.30690	0.00341
150	4.40	19.33	0.40176	0.00268
270	0.90	22.83	0.54177	0.00200
390	—2.80	26.53	0.76520	0.00196

In my former paper a preliminary experiment with ferrous iodide was described in which the coefficient appeared to be nearly constant and much smaller than here. The experiments are, however, not comparable, as in the former case the sugar solution was very strong, containing, in 250 cc., 125 grams of sugar. In such a solution the degree of dissociation of the iodide would be necessarily very different from that in a weaker solution. In the strong solution no separation of ferrous hydroxide or other compound appears, even on warming. A strong syrup is much more stable than a weak one, and the lower rate of inversion may be thus easily accounted for.

CADMIUM CHLORIDE.

One solution of cadmium chloride was tested as to its inverting power. It was made with a salt purified by several crystallizations at a low temperature, free from uncombined acid.

EXPERIMENT 25.

$CdCl_2$. 0.94*N*.

In 250 cc., fifty grams of sugar + 42.958 grams of chloride.

$A = 29.71$.

t.	a.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	21.41°	....	......	......
15	12.80	8.61°	0.14862	0.00990
30	6.59	14.82	0.30001	0.01000
60	−1.33	22.74	0.62967	0.01049
90	−4.89	26.30	0.94015	0.01044
150	−7.70	29.11	1.69475	0.01129

The rate of inversion is about as rapid as with 0.002*N* hydrochloric acid at the same temperature and same sugar concentration.

LEAD NITRATE.

A single test was made with a solution containing lead nitrate. The salt was recrystallized from a pure Schuchardt specimen and was weighed in proper amount directly.

EXPERIMENT 26.

$Pb(NO_3)_2$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 20.65 grams of nitrate.

$A = 33.70$.

t.	a.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	25.40°	....	......	......
15	22.86	2.54°	0.03403	0.00227
45	17.38	8.02	0.11803	0.00262
75	12.10	13.30	0.21800	0.00284
135	2.28	23.12	0.50314	0.00372
195	−3.63	29.03	0,85831	0.00440
345	−7.70	33.10	1.74948	0.00507

The coefficient here is found to increase very rapidly, as was noticed by Walker and Aston in their experiments,[1] which were

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[1] *Loc. cit.*

carried out with a half normal nitrate solution at 80°, but with a weaker sugar solution. The mean value they give from the results of polarization at three intervals is 0.00159, but the inversion was not carried nearly to completeness, as in the above case.

The experiments given show in a marked manner the extreme variations in the value and constancy of the inversion coefficient and the data obtained may be roughly tabulated as follows :

Potassium alum	*K* constant.
Ferrous sulphate	" increases slowly.
Ammonium ferrous sulphate	" " "
Zinc sulphate	" " "
Cadmium chloride	" " "
Manganous sulphate	" " rapidly.
Manganous chloride	" " "
Lead nitrate	" " "
Ferrous chloride	" decreases rapidly.
Ferrous bromide	" " "
Ferrous iodide	" " "

In the cases of the last three salts the values of *K* decrease very rapidly at the beginning of the heating, but become nearly constant later, finally, in fact, appearing to increase a little. This behavior seems to bear some relation to the stability of the salts in aqueous or weak saccharine solution. As was mentioned these ferrous halogen solutions became turbid in the thermostat, and the first three or four portions withdrawn in each case for polarization had to be filtered. Later, the liquids became perfectly clear under the influence of longer heating.

During the turbid stage of the reaction, owing to the temporary separation of a trace of base in insoluble form, the amount of free acid present would be relatively increased, and would therefore greatly accelerate the speed of inversion. With the clearing of the solutions on longer heating the normal hydrolysis only would obtain and then the reaction should approach in regularity that due to the presence of a small constant amount of mineral acid.

It was mentioned that the solutions with ferrous sulphate and ferrous ammonium sulphate became likewise turbid on heating. But here the very slight opalescence persisted through the whole time of heating, and was perhaps greater at the end of the reaction than at the beginning. Other experiments also show in this respect a marked difference between ferrous sulphate and chloride. In my former paper I referred to solutions of these salts which had been used qualitatively. Portions of these solutions that had not been heated are still in existence. After standing eight months in the light I find that the chloride is practically clear, while the sulphate has become much changed. The bottle contains a decided flocculent precipitate. My former experiments with a strong solution seemed to indicate that at a temperature of 100° the first slight precipitate which forms disappears, but this is not true of the weaker solutions at 85°.

The slight precipitate of ferrous chloride and other halogen compounds being temporary, while that of ferrous sulphate is apparently permanent, we should expect just such irregularities in the speed of inversion, as the experiments actually show. A solution of manganous sulphate with sugar becomes also slightly decomposed on heating, and the decomposition increases with the time and temperature. At a temperature of 100° a solution of fifty grams of sugar and ten grams of the sulphate in 100 cc. becomes so dark that an exact polarization is not possible, even after filtering. The solution in the present case is much less concentrated, but the precipitate is still marked and its formation is undoubtedly attended by the separation of a little free acid. We should therefore expect an acceleration in the rate of inversion as before.

These considerations do not aid us in explaining, however, the increase in K for manganous chloride, cadmium chloride or lead nitrate. The solutions with these salts are clear and remain so throughout the reaction. In the case of manganous chloride it must be remembered that an almost complete loss of color follows after heating. The pink fades, and in a few hours at the temperature of the thermostat becomes imperceptible in a small volume of the liquid. The color is not restored by cooling. We have here evidently a reaction in which a change takes place in the form of combination of the manganese, with a necessary alteration in the degree of dissociation of the salt.

It is true, as already said, that most of the bases under consideration form compounds with the sugars, so that we should expect from this cause a slight disturbance at least in the apparent rate of inversion. Too little is known of the optical properties of these saccharose, dextrose and levulose metallic compounds to say just what effect they would have on the rotation, but that they have some action is suggested by the results of some of the polarizations to determine the end point in the inversion. This was usually found a little below the theoretical, —8.6° for a 200 mm. tube, but in several cases it was found above after prolonged heating. This was also true of a solution of sugar with manganous chloride, which stood exposed to the light several months.

It must be remembered also that solutions of dextrose are easily oxidized, and those of levulose much more so. The dark color often seen near the end of the reaction, points to such a decomposition.

It will be recognized that a determination of the hydrolysis of many of the heavy metallic salts cannot be measured with great accuracy, because of these several disturbing influences, but a comparison of some little value in the above cases may be made by considering the results obtained at the beginning of the reactions in which the coefficient is an increasing one, and near the end of the reaction in cases where it decreased and then became nearly constant. By taking the mean of the first two values in the one case, and of the last two in the other, we obtain the second column of the table below as the most probable values of the coefficient for half-normal solutions.

In the third column is given a calculation of the extent of hydrolysis of the salts, expressed in per cents. of total salt present, and based on a comparison with hydrochloric acid acting in 0.001 normal solution at the same temperature on same amount of sugar. This comparison is at best a rough one, assuming as it does complete hydrolysis of the acid, and neglecting the effect of the excess of undecomposed salts on the rate of inversion.

	K.	Salt hydrolyzed in per cent.
Lead nitrate	0.00244	0.096
Manganous chloride	0.00095	0.035
Manganous sulphate	0.00052	0.020
Ferrous sulphate	0.00085	0.033
Ferrous ammonium sulphate	0.00068	0.026
Zinc sulphate	0.00040	0.016
Ferrous chloride	0.00164	0.063
Ferrous bromide (0.54*N*)	0.00300	0.109
Ferrous iodide	0.00198	0.078
Potassium aluminum sulphate, $\frac{N}{4}$	0.01835	1.440
Cadmium chloride 0.94*N*	0.01000	2.080

The amount of hydrolysis is small in all cases except those of the alum and cadmium chloride.

My thanks are due to Mr. S. R. Macy for much assistance in the experimental work of the above.

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CHICAGO.

DETERMINATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCK BY THE AMMONIUM ACETATE METHOD.

BY THOMAS S. GLADDING.

Received June 30, 1896.

THE oldest method of separating alumina and iron phosphates from lime phosphate is, probably, the ammonium acetate method. This has been severely criticised, and just at present seems to be under condemnation. The following investigation has convinced the writer that, when properly carried out, not only does the method give an accurate separation of iron and alumina from lime phosphate, but also gives a neutral phosphate of uniform composition from which the iron oxide and alumina present may be accurately estimated.

In brief, the method used is this. If a weakly acid solution of phosphates of iron and alumina together with a large amount of calcium phosphate be slowly poured into a strong solution of ammonium acetate made acid with acetic acid, the iron and alumina are precipitated as phosphates, upon digestion for a short time at a gentle heat. This precipitate, however, contains more or less calcium phosphate, which is removed by several reprecipitations. I shall demonstrate by experiment:

First, That upon continued reprecipitations of iron and alumina as phosphates in this manner, there is no appreciable diminution of the quantity of either finally obtained, provided there always be a large excess of phosphoric acid present.

A standard solution was made by dissolving twenty grams of ammonia alum (C. P.) in distilled water. This was slightly acidified with hydrochloric acid, in order to prevent the alumina from separating on standing, and diluted to one liter. This solution, upon being standardized, was found to contain the theoretical amount of alumina, that is,

Ten cc. = 0.0225 grams Al_2O_3.

One precipitation, in the manner described above, of the alumina in ten cc. gave

	$Al_2O_3.P_2O_5$, found.	Al_2O_3.
1	0.0545	0.0228
2	0.0549	0.0229
3	0.0546	0.0228
4	0.0540	0.0226
5	0.0545	0.0228

Three successive precipitations, in which one gram of ammonium phosphate was added before each precipitation, gave

	$Al_2O_3.P_2O_5$.	Al_2O_3.
1	0.0550	0.0230
2	0.0547	0.0229
3	0.0544	0.0227

Five successive precipitations were also tried under the same conditions, with the following results:

	$Al_2O_3.P_2O_5$.	Al_2O_3.
1	0.0536	0.0224
2	0.0530	0.0222

When, however, the excess of phosphoric acid was omitted before the reprecipitations, there was a loss of alumina.

An iron solution was made by dissolving C. P. iron wire in hydrochloric acid and oxidizing it with nitric acid. When carefully standardized it was found that

Ten cc. = 0.0296 Fe_2O_3.

Three successive precipitations, adding one gram ammonium phosphate before each, gave

	$Fe_2O_3.P_2O_5$.	Fe_2O_3.
1	0.0545	0.0289
2	0.0550	0.0291
3	0.0548	0.0290

Five successive precipitations, in the same way, gave

	$Fe_2O_3.P_2O_5$.	Fe_2O_3.
1	0.0550	0.0291
2	0.0560	0.0297

Second. That upon three successive precipitations in the presence of a large amount of calcium phosphate, as is the case in the analysis of rock phosphate, the precipitate of the phosphates of iron and alumina is sufficiently pure to be taken as such. Of the standard solutions, five cc. of each would together give a precipitate of combined phosphates about equal to that usually found in one gram of phosphate rock. The mixture so analyzed was made up as follows:

Five cc. alumina solution = 0.01125 Al_2O_3.
Five cc. iron solution = 0.01480 Fe_2O_3.
0.7000 grams calcium phosphate.

This was given three precipitations, the excess of phosphoric acid being supplied before the second and third precipitations.

	Phosphates obtained.	Al_2O_3 obtained.	Fe_2O_3 obtained.
1	0.0552	0.0115	0.0146
2	0.0540	0.0110	0.0146
3	0.0537	0.0109	0.0146
4	0.0536	0.0109	0.0146

The iron oxide was determined by volumetric method in the ignited precipitate and the alumina by subsequent calculation.

In addition twenty cc. alumina solution containing 0.0450 grams Al_2O_3, together with 0.700 grams calcium phosphate, were given three successive precipitations in the same way with the following results:

	$Al_2O_3.P_2O_5$ obtained. Grams.	Al_2O_3 obtained. Grams.
1	0.1092	0.0456
2	0.1074	0.0449

In order to prove that the aluminum phosphate precipitated was the normal phosphate, the ignited precipitates were fused, and the phosphoric acid in them estimated.

	$Al_2O_3.P_2O_5$.	P_2O_5 obtained.	Al_2O_3 by diff.	Al_2O_3 by calc.
1	0.0538	0.0313	0.0225	0.0225
2	0.0533	0.0312	0.0221	0.0223

The phosphate of alumina is multiplied by the factor 0.418 to obtain the alumina.

Therefore, in determining iron oxide and alumina in phosphate rocks proceed as follows:

Four grams of the finely ground sample, previously freed by a magnet from any metallic iron derived from the iron mortar used in grinding the sample, are digested for half an hour, at a temperature just below the boiling-point, with about thirty cc. dilute hydrochloric acid (1–1). This will prevent the solution of any pyrites if present. Filter and wash thoroughly into a 200 cc. flask, add a little nitric acid, and boil to oxidize the iron, cool, and fill to mark with water. Take two portions, fifty cc. = one gram, twenty-five cc. = one-half gram, and proceed with each as follows:

Almost neutralize the solutions with strong ammonium hydroxide until the precipitate formed dissolves with difficulty, and thoroughly cool by placing the beaker in a dish of cold water. The neutralization is then completed by carefully adding dilute ammonium hydroxide until the precipitate remains permanent, then just dissolve by adding dilute hydrochloric acid, drop by drop, stirring well. Have ready in another beaker a mixture of fifteen cc. of a strong solution of ammonium acetate (made by neutralizing thirty per cent. acetic acid with strong ammonium hydroxide) and five cc. of acetic acid. Carefully pour the cold faintly acid solution of phosphates in a fine stream into this mixture, stirring all the while. Digest at 60° C. from one-half hour to one hour, until the supernatant liquid is clear and the flocculent precipitate is well settled to the bottom.

Filter and wash the precipitate once with a ten per cent. ammonium acetate solution, merely rinsing out the beaker in which the precipitation was made. Dissolve the precipitate from the paper into the same beaker with a few cubic centimeters of hot dilute hydrochloric acid (1–4). Use as little acid as possible in order to keep the bulk of the solution small. Add one gram of ammonium phosphate, neutralize with ammonium hydroxide and add hydrochloric acid until the precipitate just dissolves as before and pour into a mixture of fifteen cc. ammonium acetate solution and five cc. acetic acid. Digest at 60° C. for one-half to one hour and filter, and wash once with the ten per cent. ammonium acetate solution. Redissolve and repeat the precipitation, being careful to again add one gram of ammonium phosphate to the solution, in order that there be a sufficient excess of phosphorus pentoxide to precipitate all the alumina as a neutral phosphate. Wash the precipitate three times with dilute ammonium acetate solution.

Take the filter, while wet, from the funnel and ignite in a tared platinum capsule, using a very low flame until the filter paper is thoroughly charred. The heat is increased gradually until the paper is completely consumed, and finally the blast lamp is used for a minute. Weigh as combined phosphates of iron and alumina. The iron is determined volumetrically in the solution of the weighed precipitates. The iron oxide present in the rock is also determined separately by volumetric process, preferably the bichromate method, in a solution of five grams of the rock in dilute hydrochloric acid (1-1), reducing all iron to protoxide and titrating with bichromate.

The ignited precipitate from one of the duplicate precipitations may, if desired, be dissolved and subjected to a fourth precipitation and the filtrate tested for lime by adding ammonium oxalate and heating. My thanks are due to our assistant, Thomas Brown, Jr., for valuable aid in the above analytical determinations.

LABORATORY OF STILLWELL & GLADDING,
NEW YORK CITY.

A NEW METHOD FOR THE ESTIMATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCK.

BY THOMAS S. GLADDING.

Received June 30, 1896.

THE method for the separation of alumina from phosphate of lime by three successive precipitations with ammonium acetate is tedious, though accurate if proper precautions be taken, as shown in the preceding paper on this subject.

The following modification suggested itself as saving both time and labor. This modification consists of the separation of alumina from calcium phosphate and iron by means of its solubility in an excess of caustic potash. To demonstrate the accuracy of this method, a solution of ammonia alum, twenty grams in a liter, was used as in the previous experiments, ten cc. containing 0.0225 grams Al_2O_3. The caustic potash solution was made by dissolving 500 grams of caustic potash in distilled water and diluting to one liter. Chemically pure caustic potash, purified by barium, was used and was carefully tested for alumina, as much so-called chemically pure potash contains an appreciable amount of alumina.

To a solution of mixed phosphates of alumina, iron, and lime were added fifteen cc. of the C. P. potash solution. The mixture was digested for an hour at a temperature of 70° C., with occasional stirring. It was then filtered, the filtrate neutralized with hydrochloric acid, and the alumina was precipitated as a phosphate with ammonium acetate as described in my ammonium acetate method.

Ten cc. standard alumina solution + 0.030 gram iron oxide + 0.500 gram calcium phosphate gave

	$Al_2O_3.P_2O_5$ found. Grams.	Al_2O_3. Grams.
1	0.0538	0.0225
2	0.0542	0.0227
3	0.0543	0.0227
4	0.0543	0.0227

Comparative tests were made on phosphate rocks between this method by solution in C. P. potash and by three successive precipitations with ammonium acetate.

	By new potash method. Al_2O_3 found. Per cent.	By acetate method. Al_2O_3 found. Per cent.
1	1.05	1.03
2	1.19	1.16
3	1.86	1.61
4	1.07	0.99
5	1.88	1.98

These results show the accuracy of this method, both in obtaining a known amount of alumina and in showing close agreement with results by the acetate method.

This method has been in use in our laboratory for over a year. A reprint of an article by M. Henri Lasne[1] has just been received, giving a method for the separation of alumina from phosphates of iron and lime very similar to this. M. Lasne uses caustic soda instead of potash and precipitates his aluminum phosphate with ammonium hyposulphite instead of ammonium acetate. I have made a few comparative tests by my method and that of M. Lasne and find closely agreeing results.

Using ten cc. standard alumina solution + 0.500 grams calcium phosphate I found

	By my method.		By Lasne's method.	
	$Al_2O_3.P_2O_5$. Grams.	Al_2O_3. Grams.	$Al_2O_3.P_2O_5$. Grams.	Al_2O_3. Grams.
1	0.0542	0.0220	0.0540	0.0226
2	0.0538	0.0225	0.0533	0.0223

In the analysis of a phosphate rock I found

By my method. Al_2O_3 found. Per cent.	By Lasne's method. Al_2O_3 found. Per cent.
1.75	1.73
1.80	...

The detailed method used in my work is as follows: Treat the finely ground rock phosphate with a magnet to remove any metallic iron derived from the iron mortar used in the preparation of the sample. Dissolve four grams of the rock in thirty cc. dilute hydrochloric acid (1–1), heating just below the boiling-point for half an hour. This prevents the solution of pyrites. Filter into a 200 cc. flask, add a few drops of nitric acid, and boil to oxidize the iron, cool and dilute to mark. Take fifty cc. containing one gram of rock and run into twenty cc. of the solution of C. P. caustic potash. Digest for an hour at 70° C., stirring occasionally. Let the precipitate settle and filter on a large paper, first decanting the supernatant liquid on the paper and finally washing on the precipitate. Wash two or three times with hot water.

To the filtrate add one gram of ammonium phosphate, acidify with hydrochloric acid, add ammonia until a permanent precipitate is formed and dilute hydrochloric acid, drop by drop, until it is just dissolved. Add a mixture of fifteen cc. neutral ammo-

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[1] From the *Bulletin de la Société chimique de Paris*, [3] 15, 118, *1896*.

nium acetate solution and five cc. acetic acid (thirty per cent.) and digest for half an hour at 70° C., by which time the precipitation is complete.

Filter, washing five or six times with hot ammonium acetate solution (ten per cent.), stirring up the precipitate with the jet each time. Ignite with a low flame until the paper is charred, increase the heat, and, when the paper is completely consumed, blast for a minute. The precipitate is the normal aluminum phosphate and its weight multiplied by the factor 0.418 gives the Al_2O_3.

The iron oxide is determined volumetrically, preferably by the bichromate method, in a solution of the precipitate of iron oxide and calcium phosphate thrown down by the caustic potash. It is also determined separately, by the same method, in a solution of five grams of the rock in dilute hydrochloric acid (1–1).

My thanks are due to Mr. H. E. Cutts, A.M., for valuable assistance in the above investigation.

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SOME THOUGHTS ABOUT LIQUIDS.

BY CLARENCE L. SPEYERS.

Received June 3, 1896.

CONSIDER an empty closed space. Imagine a quantity of liquid put into it, enough to fill the space with vapor and leave some liquid over. A portion of the liquid changes into vapor and passes into the previously empty space above the liquid and continues doing so until the pressure of the vapor reaches a certain value, when the vaporization ceases.

The usual way of explaining this vaporization starts out by assuming that, with the exception of the surface, the liquid is perfectly homogeneous in a physical sense. That is, there is not a single particle of the liquid which for any appreciable length of time is different from any other particle, but of course, spaces between the particles of liquid are recognized. At the surface of the liquid, however, a distinction is to be made. For outside the surface, the activities are different from those within the surface, otherwise there would be no boundary. So that the particles at the surface are subjected to activities that are different in different directions, and consequently the particles so situated will behave differently from those particles entirely within the liquid.

In van der Waal's theory the mutual attractions of the particles of the liquid are considered as the restraining force to keep the particles more or less together. This assumed force must be very great—a good many hundred atmospheres. Inside the liquid, below the surface, the attraction is equal in all directions, but at the surface it acts only in one direction, inwards, normal to the surface. Now, although the force restraining the particles of liquid from separating is so great, yet the theory of common acceptance assumes that some particles do break away from the mass of the liquid and form vapor. The liquid is said to evaporate. It is hard to accept this view of the case, particularly as electrical results point towards an exceedingly quiet condition of affairs within the body of liquids.

Still admitting that the particle does break away from this attraction, it cannot do so without an abundant supply of energy, which must be accounted for. It does not seem right to find this energy in the heat of vaporization, for a particle of liquid will voluntarily take heat energy from the liquid to do this work, and so go off as a particle of vapor at the sacrifice of the energy of the liquid.

It is not possible to prevent a liquid from vaporizing by refusing to give it heat; it will take the required heat from the rest of the liquid. In other words, the condition of the liquid state strongly favors vaporization.

The common theory tries to get over this difficulty by claiming that the particle which gets away, gets away by virtue of an inherent kinetic energy greater than the attractic energy of the particles of liquid, that is, greater than the force denoted by van der Waal by $K = \frac{a}{v^2}$, and that it possesses this excess of kinetic energy in the body of the liquid, before it got away, and that it got away only by virtue of this excess of kinetic energy. Similarly with all particles in the liquid having a kinetic energy greater than the energy of the mutual attraction of the particles the one for the other.

Still again admitting that the particles with the greater kinetic energy do succeed in getting out, we shall have to look for a loss in the mean kinetic energy of the liquid, to be shown by a fall in temperature. This is the case and in this respect theory and fact agree, for vaporization lowers the temperature of the liquid. In regard to the vapor, however, we meet with this difficulty. The kinetic energy of a given particle while within the liquid might be just sufficient to carry it beyond the sphere of action of the liquid, in which case the kinetic energy remaining to the particle after reaching freedom would be little and its temperature should be less than that of the liquid; on the other hand, the kinetic energy of the given particle might be far more than sufficient to carry it beyond the sphere of action of the liquid and then the kinetic energy that the particle still has after reaching freedom, should be more or less great. Consequently a particle of vapor, just after getting out of the liquid, might have any temperature between absolute zero and ∞°, in some cases perhaps touching the inferior limit, but of course, never reaching the superior limit. As a consequence of this we should expect to find the temperature of the vapor very different from that of the liquid; but this is not the case, observation has never shown that the temperature of the vapor is very different from that of the liquid which produces it. However, this is not a fatal objection, for we can assume that the mean of kinetic energy, while within the liquid, of the particles that escape from the liquid is of just such a value that after they have all got out of the liquid, the diminution of their mean kinetic energy, due to the attraction of the liquid, brings the kinetic energy left to them to the mean kinetic energy of the liquid. This seems like a forced explanation, very forced, but still perhaps not more so than the theory it is intended to help.

However, we are not yet out of the difficulty. For what becomes of the kinetic energy lost by the particles as they pass out into the vapor state?

So far as the liquid is concerned, it may take the form of heat energy and so lessen the quantity required to supply the deficit due to the escape of the particles with great kinetic energy from the liquid. But all of the lost kinetic energy cannot be absorbed here in the liquid, some must also go into the vapor particles. It may take the form of heat, as we have suggested in the case of the liquid, but then we have to assume that the kinetic energy, while within the liquid, of the particles that escape is of just such a value that, after they have all got out of the liquid, the diminution in their mean kinetic energy, due to the attraction of the liquid plus this correction, brings the kinetic energy left to them to the mean kinetic energy of the liquid, which is absurd.

Nor does the attractive energy seem to be stored up as potential energy, as in the case of a stone raised above the surface of the earth, for there is no evidence at all that a vapor particle tends toward the liquid as the stone does toward the earth. When the particle gets out of the liquid it seems to be utterly indifferent to the liquid.

Of course the mutual attraction that all bodies have for each other is left out of account.

Nor is there any sign of electrical action, at least if the experiments made up to the present time are conclusive.

There are then a good many very serious objections to the present theory of vaporization.

First, in accounting for the escape of the vapor.

Second, in accounting for the temperature of the vapor.

Third, in accounting for the kinetic energy lost by the particle in getting through the surface of the liquid and beyond the sphere of action of the liquid particles.

Let us now turn our attention to another view of the case. Consider a liquid which has no vapor-tension of its own, a non-volatile liquid, but which can dissolve gases. The liquid and gas are supposed to act according to Henry's law; that is, the ratio of concentration of the gas in the liquid part and in the gaseous part is to be constant, or in other words, the quantity of gas dissolved by the liquid is to be proportional to the pressure on the gas.

In such a system there are three constituents to be considered. The gas in the gaseous state, the gas in solution, and the solvent.

The state of the dissolved gas is not positively known, but in all probability it is in a state corresponding to a gas under high pressure for these reasons. In the first place, it is hard to see how a substance like nitrogen, for example, could be in the liquid state in a solution of moderate concentration. Great pressure is required to liquefy it even when the temperature is far below the ordinary temperature, and at the ordinary temperature it has hitherto been found impossible to liquefy nitrogen, no matter how great the pressure. Still it would be consistent with the ordinarily accepted theory to claim that the attraction of the particles of solvent could overcome the great internal energy of the gas particles and bind them down to a lesser activity and produce the liquid state. But on the other hand, modern investigation has very plainly shown that dissolved substances have a gaseous nature; the particles of the dissolved body are free to assert their physical individuality. That is to say, the solvent is to be considered rather as a medium through which the dissolved body can be put under certain conditions, the conditions varying to some extent with each solvent, but all solvents having the common action of allowing a sort of gasification of the substance dissolved, In general the solvent is not to be considered as a substance which unites with the dissolved body, forming a new compound. For example, consider anhydrous calcium chloride. When this is treated with water there is strong evidence of combination of the two to form calcium chloride hydrate. If the quantity of water is properly adjusted the whole of it combines with the calcium chloride, forming a crystallized hydrate. If this crystalline substance is treated with more water, solution begins and during this process, which is the real solution, there is no sign of chemical action. It is true, some scientists, particularly those of the English school, have denied this and have claimed to find strong evidence of a chemical action during the process of solution, but so far all such claims have turned out to be mere opinions based upon very doubtful measurements.

So we are to look upon solution as being a change in which the dissolved body is gasified. Sometimes a further change, electrolytic dissociation, takes place, but that is outside the scope of this article. It is in best accordance with what we know about other bodies to assume that the dissolved nitrogen is in the form of a gas, and to recognize two states in the solution, the gaseous state of the substance in solution and the liquid state of the solvent.

Let us now pass on to a liquid which gives off vapor. The purpose of this article is to justify the view that this vapor behaves toward the liquid just as the nitrogen did toward its solvent in the previous case, of course, with the obvious limitations due to identity in the composition of vapor and liquid.

The boundary dividing vapor from liquid is commonly supposed to be at the surface of the liquid, although the possibility of a differentiation occurring inside the liquid does not seem to be denied, for so far as could be found out by the writer, the question of such a possibility has never been raised.

The tendency for a liquid to vaporize and the pressure of its saturated vapor is evidently a function of temperature only. There seems to be no reason, therefore, why the fluid should not separate into vapor and liquid within the surface of the liquid. That it is possible for vapor to be there follows from what we know about the gaseous nature of the substances in solution. It is rather odd that this view of the case was not adopted at the outset by chemists.

According to this view, when we heat a liquid we increase the energy of translatory motion, we increase its temperature. But besides this we cause a separation of some of the liquid particles from the body of the liquid, bringing them into a state of freedom, such that they can behave just as the particles of any other substance would do in the same solvent. This of course will consume considerable energy. These free particles of vapor in the liquid we shall call dissolved vapor particles. So that on heating in liquid we produce dissolved vapor and raise the temperature of the whole fluid; possibly we do more, but at any rate we do these two things. Now by Clausius' theory of the true specific heat, the heat required to raise only the temperature of a unit mass of substance one degree, should be the same whatever the state of the substance may be, and the value of the true specific heat should be the value of the specific heat when the substance is in such a state that the heat added can only change its temperature and not do any other internal work, namely when the substance is in a state of gas. So if we subtract from the specific heat of the liquid the specific heat of the gas, the remainder should be the heat consumed in other internal work, and if no other internal work is done than the rise in temperature and production of dissolved vapor, we should get the heat required to change some of the liquid into dissolved vapor. The quantity changed into vapor however is so far unknown.

The dissolved vapor is supposed to be produced until its energy balances the energy of the liquid part.

Suppose, for example, we heat one gram of water one degree in a closed vessel which does not allow it to give off gaseous vapor. The heat required will be about one calorie, depending upon the initial temperature; one calorie is near enough for our purpose. A part of the heat goes to increase the translatory motion and is the true specific heat; but another part, perhaps the whole of the remainder, we claim goes to produce dissolved vapor. Subtracting the true specific heat of water, namely the specific heat of water vapor at a high temperature = 0.4776, we have left 0.5224 as the heat required to change a certain unknown quantity of water into dissolved water vapor, provided that no internal work is done but the two kinds we have considered. We shall assume this to be true until there is evidence of a more complex change.

Now suppose a space be made over the liquid, to let a certain quantity, say one per cent., be changed into gaseous vapor. It is of course evident, if the theory be at all tenable, that the vapor arising from the liquid comes from the dissolved vapor and bears to the dissolved vapor the same relation that the nitrogen did to the dissolved nitrogen. Comparatively little heat should be required in this process, for most of the change has been effected in the body of the liquid. Whatever is required here should be looked upon as the true heat of vaporization; that which is usually so called we are to consider as including the heat required to change a unit mass of liquid into dissolved vapor as well as the heat required to vaporize the unit mass of dissolved vapor. The two quantities should evidently be kept carefully separated.

Let us now proceed to determine the concentration of the dissolved water vapor. As the dissolved water vapor is supposed to be like a dissolved gas, Henry's law should give us some aid in finding the quantity. We might assume, in the first place, that the relative vapor density of a liquid at two different temperatures gives the relative osmotic pressures of the dissolved vapor at those temperatures, were it not for the uncertainty as to how the temperature affects the pressure of the vapor and the osmotic pressure of the dissolved vapor. It would not do to assume that each was affected in the same degree by a change in temperature. But our theory does allow us to claim in the case of a given liquid at a constant temperature that two different vapor-tensions will correspond to two different concentrations of the dissolved vapor by Henry's law, and that the relative vapor-tensions are as the relative concentrations of the dissolved vapor. Now we can change at will, within quite a wide range, the vapor tension of a liquid without changing its temperature and without introducing any complications.

To understand this let us refer back to the original conception of the dissolved vapor. If we have liquid water in a vessel with any number of gases under moderate pressure, the partial pressure of the saturated water vapor will be very nearly the same as if it alone were present in the space containing the gases. So when we dissolve a substance in water it would seem as if we might argue that the osmotic pressure of the dissolved substance should not affect the pressure of the dissolved water vapor. However the conditions in the two cases are very different. In the first case there is abundant space for the water vapor so that all that is necessary is time for the concentration of the water vapor to reach the same value no matter how many gases may be present, provided of course that the total pressure be not very great. When however the total pressure is great, the vapor-tension of the liquid diminishes very much. This is just the condition that holds in a liquid. The volume available for a dissolved substance is very small, and so anything put into this space will very materially lessen the space available for the dissolved vapor, particularly as the quantities used in solutions are generally very much greater than those used in the gaseous state.

Suppose we have n gram-molecules of a substance whose molecules do not dissociate on dissolving, say sugar, and dissolve it in water. Let ν be the number of gram-molecules of dissolved vapor after the n gram-molecules of substance have been dissolved, then the total number of gram-molecules present in solution will be $\nu+n$, and the relative number of gram-molecules of substance dissolved to total number of gram-molecules in solution is

$$\frac{n}{\nu+n}.$$

Now let j be the concentration of the dissolved vapor when alone in the liquid, and j' its concentration after the new substance has been added, in this case the sugar. $j-j'$ will be the decrease in the concentration of the dissolved water vapor due the addition of the n gram-molecules of sugar, and since a gram-molecule of all substances occupies the same volume, the decrease in concentration $j-j'$ will be the same whatever the substance dissolved may be, provided the same number of gram-molecules be taken in each case, or the decrease in concentration of the dissolved vapor is proportional to the number of gram-molecules dissolved in a certain fixed volume of solution. If the temperature is constant the concentration of the dissolved water vapor cannot rise above the value j, which it has when only dissolved vapor is present; when we try to get above this value the dissolved vapor turns to liquid water. Hence the number of gram-molecules in a unit volume must be fixed, if the temperature is constant, that is

$$\nu+n = \text{constant.}$$

We have, therefore,

$$\frac{j-j'}{j} = \alpha \frac{n}{\nu+n} \tag{1}$$

where α is a constant.

$j-j'$ can be calculated by van't Hoff's law, and n is known, but the other quantities are not, so neither j or ν can be calculated from this equation.

There is however another relation that can be deduced.

The concentration of the dissolved vapor is measured by its osmotic pressure.

Let π, ϕ, be respectively osmotic pressure and osmotic volume of the dissolved vapor, when it alone is present; π', ϕ', the corresponding quantities when a substance is in solution; p, v, the pressure and volume of the vapor in contact with the pure solvent; p', v', the corresponding quantities when a substance is in solution.

Consider an isothermal reversible cycle composed of the following parts.

• By means of a semipermeable diaphragm let a gram-molecule of dissolved vapor pass from the pure solvent, the work will be

$$-\pi\phi = -RT.$$

Let the gram-molecule of vapor expand until it has a pressure of π the work will be

$$-\int_{\pi'}^{\pi} \phi d\pi = -RTl\frac{\pi}{\pi'}.$$

Let it then pass into the solution; the work will be

$$+\pi'\phi' = +RT.$$

Let x gram-molecules pass out of the solution in the form of vapor; the work will be

$$-xp'v' = -xRT,$$

where x denotes the number of gram-molecules of gaseous vapor necessary to make one gram-molecule of dissolved vapor.

Let the x gram-molecules of vapor be compressed until the pressure equals p; the work will be

$$+x\int_{p'}^{p} vdp = +xRTl\frac{p}{p'}.$$

Let the x gram-molecules be driven into the pure solvent; the work will be

$$+xpv = +xRT.$$

Thus the cycle is completed. The quantity of solution is supposed to be so large that the addition and removal of the quantity of the solvent used in the cycle will have no appreciable effect upon the concentration of the solution.

The sum of the changes of energy must be zero, so

$$-RT - RTl\frac{\pi}{\pi'} + RT - xRT + xRTl\frac{p}{p'} + xRT = 0;$$

Hence,
$$\frac{\pi}{\pi'} = \left(\frac{p}{p'}\right)^x \tag{2}$$

We shall assume that x equals 1; there is no good reason for thinking otherwise, and the simplicity in the structure of dissolved bodies favors this assumption.

From the theory we have

$$\frac{j}{j'} = \frac{\pi}{\pi'} \tag{3}$$

We have therefore from 1 through 3 and 2,

$$1 - \frac{p'}{p} = \frac{p - p'}{p} = \alpha\frac{n}{\nu + n} \tag{4}$$

but from experiment,

$$\frac{p - p'}{p} = \frac{n}{N + n} \tag{5}$$

where N is the number of gram-molecules of liquid in which n gram-molecules of substance have been dissolved.

Hence,

$$\alpha\frac{n}{\nu + n} = \frac{n}{N + n} \tag{6}$$

Now as equation (6) is true for any small value of n it will be true for a value so small in comparison with ν and N, that it may be neglected, and so

$$\frac{\alpha n}{\nu} = \frac{n}{N},$$

or,

$$\alpha = \frac{\nu}{N} \tag{7}$$

Substituting in (6) we have

$$\frac{\nu}{N}\frac{n}{\nu+n}=\frac{n}{N+n},$$

or,

$$\nu=N \tag{8}$$

That is, the concentration of the dissolved vapor is the same as the concentration of the liquid, or in other words, all the solvent is to be considered as dissolved vapor.

This is very interesting, for it is in effect the same conclusion that van der Waals reached in his celebrated treatise, though he pursued a very different method.

It would seem from this result that matters were left in about the same state that they were in at the outset; that the view of dissolved vapor was no better than the old view, which claimed that the change into vapor took place only on the surface of the liquid. But we have really gained several things.

In the first place we have found that reasoning from the analogy that a dissolved gas and the same gas in contact with the solvent bears to the liquid and its vapor we got to the idea of dissolved vapor and from that to a result in agreement with a much older theory.

Secondly, we have found that a liquid is to be looked upon as a condensed gas, not simply condensed in the sense that it is a matter compressed into smaller space, but condensed in the sense that the gaseous activity, pressure, is carried into the liquid condition, and we are to treat a liquid as we would a gas.

Thirdly, it follows from this view that a substance dissolved is simply brought into the same condition that the liquid is in, and consequently should have the same property of exerting an osmotic pressure that the liquid has.

Finally, what causes the condensed gaseous state? Until this is answered the problem of liquid and gas is essentially unsolved. That it is due to an attraction between the molecules, is hardly possible, as we have seen at the beginning of this paper. Indeed so soon as we begin to reflect upon the complications that are introduced the moment the ideas of molecule and attraction are brought into an investigation, and these complications are all the time increasing instead of diminishing, the more natural and simple appears the view of Ostwald that we shall find a better solution of such problems in energy alone, matter being only a collection of energies in space.

Now as to the value of the osmotic pressure in some liquids. In 1000 cc. of water there are

$$\frac{1000}{18} = 55.55 \text{ gram-molecules.}$$

Every gram-molecule at 25° C. (= 298° absolute temperature) in 1000 cc. has a pressure of

$$\frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \text{ m.}$$

Hence for the 55.55 gram-molecules of water we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{18} = 1024 \text{ meters of mercury.}$$

In 1000 cc. methyl alcohol there are

$$\frac{1000}{32} \cdot 0.79 \text{ gram-molecules,}$$

and hence for methyl alcohol we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{32} \cdot 0.79 = 455 \text{ m.}$$

In 1000 cc. ethyl alcohol there are

$$\frac{1000}{46} \cdot 0.79 \text{ gram-molecules,}$$

and hence for ethyl alcohol we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{46} \cdot 0.79 = 316 \text{ m.}$$

In 1000 cc. propyl alcohol there are

$$\frac{1000}{60} \cdot 0.80 \text{ gram-molecules,}$$

and hence for propyl alcohol we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{46} \cdot 0.80 = 249 \text{ m.}$$

In 1000 cc. chloroform there are

$$\frac{1000}{119}.\ 1.52 \text{ gram-molecules,}$$

and hence for chloroform we have

$$\pi = \frac{22222}{1000}.\frac{298}{273}.\ 0.76\frac{1000}{119}.\ 1.52 = 235 \text{ m.}$$

In 1000 cc. toluene there are

$$\frac{1000}{92}.\ 0.88 \text{ gram-molecules,}$$

and hence for toluene we have

$$\pi = \frac{22222}{1000}.\frac{298}{273}.\ 0.76\frac{1000}{92}.\ 0.88 = 176 \text{ m.}$$

RUTGERS COLLEGE.

[CONTRIBUTIONS FROM THE LABORATORIES OF THE SCHOOL OF MINING, KINGSTON, ONTARIO.]

VOLUMETRIC ESTIMATION OF LEAD.

BY FRED. J. POPE.

Received May 21, 1896.

QUITE frequently of late, the attention of readers of chemical journals has been directed to various methods[1] for estimating lead volumetrically. But, while some of these methods are superior to any previously made public, yet, for none of them is that degree of accuracy claimed which is so essential in a reliable quantitative operation. The chief objection to all of these methods is the use of an outside indicator. However, by using an inside indicator and modifying slightly the usual preliminary steps (necessary for the conversion of the ore into the sulphate) results have been obtained by the writer which are quite satisfactory.

The operation may be briefly outlined as follows: The lead is first converted into lead sulphate, then into lead acetate. Excess of standard potassium bichromate is added, which precipitates the lead as lead chromate. The unused potassium bichromate is reduced by excess of standard arsenious acid, and this latter

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[1] This Journal, 17, 901; *Engineering and Mining Journal*, July 7, 1894.

titrated with iodine solution, using starch paste as an indicator.

PREPARATION AND STANDARDIZING OF SOLUTIONS.

Taking tenth normal solution of iodine as the standard, 4.995 grams of arsenious acid per liter and 4.763 grams of potassium bichromate per liter give standard solutions of equivalent value per equal volumes.

Iodine.—12.7 grams are dissolved in concentrated potassium iodide solution and made up to one liter.

Arsenious Acid.—Dissolve 4.95 grams in twenty or thirty cc. of saturated, filtered solution of sodium carbonate, gently warming. If too strong heat is applied the arsenious acid cakes and dissolves with difficulty.

By means of a burette accurately measure ten to fifteen cc. of arsenious acid solution, running it into a large porcelain dish. Acidify faintly with sulphuric acid, add fifty cc. saturated solution of pure sodium bicarbonate, add starch paste and titrate with the iodine.

Potassium Bichromate.—Weigh out approximately five grams, dissolve and make up to one liter. Remove twenty-five cc. to a porcelain dish, add fifty cc. of the standard arsenious acid and proceed with titration as already indicated.

Note.—Since all commercial sodium bicarbonate will decolorize more or less iodine, it is well in neutralizing to get the neutral point exactly. When this is attained, add fifty cc. sodium bicarbonate and deduct its iodine value from the quantity consumed.

The Operation in Detail.—Take from three to seven grams of ore, according to its richness in lead. Place this in a deep three-inch porcelain dish, thoroughly moisten it with water, cover the dish with a watch-glass and for each gram of ore used add four to five cc. of a previously prepared mixture of two parts by volume of sulphuric acid, three parts by volume of nitric acid and one part by volume of water. When the reaction, which first results, diminishes, evaporate as nearly to dryness as is possible without spurting. Cool, fill the dish with cold water, stir well and allow to settle for two or three minutes. Filter and wash with cold water until most of the acid is removed. Convey the filter paper with the precipitate to a 300 to 400 cc. beaker or Erlenmeyer flask and neutralize any remaining acid with dilute ammonia. To the porcelain dish add ten to fifteen cc. strong ammonium acetate, made decidedly acid with acetic acid. Add an equal volume of water and boil for two or three minutes, washing the sides of dish so as to remove any remaining lead sulphate. This solution is then added to the flask containing the precipitate and the whole boiled from seven to ten minutes with frequent stirring. Cool, neutralize with ammonia, add 100 cc. of standard potassium bichromate, stirring well. Filter into a half liter measuring flask, moistening the filter paper with dilute ammonia or ammonium acetate. Wash precipitate as much as is possible in the flask, using hot water. The filtrate make up to the mark, and for titrating remove 100 cc. to a large one and one-half liter porcelain basin. Add ten to twenty cc. (or less if ore is rich in lead) of standard arsenious acid. Make decidedly acid with forty per cent. sulphuric acid and stir until the yellow color disappears or the liquid has a greenish tinge. A large excess of sulphuric acid is to be avoided. Neutralize with saturated solution of sodium bicarbonate and then add an excess of fifty cc. If the solution has a deep greenish tinge dilute it with distilled water. Finally add starch paste and titrate with standard iodine solution.

As a test of the accuracy of method, five portions of pure lead sulphate were acted upon and the following results obtained:

Grams taken.	Grams found.
1.0	1.000568
1.1	1.099375
1.2	1.200467
1.3	1.300673
1.4	1.399571

With a specimen of galena containing quartz and calcium carbonate, the writer obtained the following percentages:

Grams taken.	Per cent. lead found.
0.7	81.89
0.7	81.96
0.71	81.94
0.68	81.90

As a test of the method in the hands of inexperienced operators, it was outlined and explained to four junior students, who with the galena ore already mentioned, obtained the following results:

Grams taken.	Per cent. lead found.
R. H = 0.7	81.86
G. E. R. = 0.7	81.78
S. D. {1 = 0.7	82.00
S. D. {2 = 0.85	81.89
G. E. S = 0.7	81.95

With another ore containing five per cent. of copper, twenty-six per cent. of iron, quartz and gypsum, one of the students obtained the following results:

Grams taken.	Per cent. lead found.
3.0	15.89
3.5	16.01
4.0	15.97

ESTIMATION OF SULPHIDES IN CALCIUM CARBIDE.

BY FRED. J. POPE.

Received May 21, 1896.

A WEIGHED quantity of calcium carbide was conveyed to a dry Erlenmeyer flask provided with a stop-cock funnel and a delivery tube, which latter led to a ten ounce wash bottle, this in turn being connected with a smaller one. The wash bottles contained 150 cc. lead acetate of known strength (about tenth normal). By means of a stop-cock water was carefully added until there was no further evolution of acetylene. On the reaction ceasing, twenty-five to forty cc. sulphuric acid (1 : 3) was run into the flask and the whole gently boiled, the liberated hydrogen sulphide passing into the wash bottles and precipitating the lead as lead sulphide. When the reaction had ceased the flask and liquid was washed free of hydrogen sulphide by a current of air and the contents of wash bottles filtered. The filtrate containing unconsumed lead acetate was made up to a half liter. To 100 cc. of this solution were added standard potassium bichromate, arsenious acid, etc., (as indicated in preceding article) and total amount of unconsumed lead acetate estimated. The difference between this amount and the quantity of lead acetate started with gave amount precipitated by the hydrogen sulphide from which the sulphur existing as sulphide was calculated.

Grams calcium carbide taken.	Per cent. sulphur found.
2.4492	3.37
3.1234	3.57

No attempt was made to check the application of the method. It is obvious that the impure calcium carbide may have evolved other products capable of removing lead from the solution. It is the writer's intention to investigate this and other points connected with this method.

NOTE ON THE PRESENCE OF OIL IN BOILER SCALE.[1]

By Charles A. Doremus.

Received June 9, 1896.

IT is difficult to remove cylinder oils, whether pure mineral or mixtures of mineral and animal from condensed exhaust steam. The practice of recovering steam either for the preparation of distilled water or for boiler feed water is now so general that opportunities for observing the troubles attending the procedure are not wanting.

This sample of water was obtained by melting the "core" of cakes of artificial ice. The sediment is fine, flocculent and of red color. When removed from the water and dried it is pulverulent. There is very slight evidence of oil in the dry mass, the moist sediment does not appear oily. The large proportion of oil extracted by ether shows how inefficient the filters were in purifying the condensed steam. Yet very great pains were taken at the ice plant to secure pure distilled water, and there was no visible oiliness in the water as it flowed to the freezing cans. Here however the corrosive action of the distilled water on the galvanized iron produced a mass of iron and zinc hydrates which in being pushed to the centre by the gradual formation of ice gathered the oil and carried it to the core.

Another specimen is one obtained from a steamboat trafficing on the Hudson river and using salt or brackish water in the surface condensers. The boilers were said to be foul with masses

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[1] Read before the New York Section. June 5th, 1886.

of oil coating the sides and tubes. Having determined the presence of the salts of sea water in the boiler, due to leaky condensers, a treatment was suggested which caused a fine precipitate. This precipitate gathered the oil in masses easily brushed from the crown sheets. When this mass is treated with ether a dry powder remains and oil dissolves.

A third specimen sent for examination from a large plant in Chicago, evaporating 2500 gallons of filtered river water and 25,000 condenser water every twenty-four hours. Lubricating oil, mineral with ten per cent. animal, is freely used, and the fine clay in the water has together with some incrusting ingredients, caused the oil to form into balls.

The next two specimens are in striking contrast to the foregoing. This is light colored, one-quarter inch thick, has a layer of dense nature near what must have been the heated surface on which the scale formed while the bulk of the incrustation is fibrous. The incrustation consists of calcium carbonate and sulphate, with which is intermingled clay and organic matter, the latter partly oil.

The general appearance of the next sample is quite different. The incrustation is in thin sheets about three-sixteenths inch thick, of light slate color, and made up of alternating layers of deposit of varying hardness. The ingredients are again calcium carbonate and sulphate and clay, while there is much organic matter. This can be separated from the mineral in great part by a little acid. The presence of oil is then noticeable. The boiler of this plant is fed with Lake Michigan water and condenser water. The latter goes directly to the hot well of twenty barrels capacity. While there are no oil filters the boiler is provided with a skimmer, which draws off floating materials from just below the water line. The lubricating oil used is mineral with fifty per cent. animal.

Notwithstanding the skimmer, the scale has formed and baked into a hard mass. It is highly non-conducting. It can be held by the fingers quite near to where a portion is heated in a Bunsen flame, the heat of which distils out and ignites the oil. A few pieces of this scale heated in an improvised retort made from a test tube yield quite a gas flame. The presence of oil to the extent of from twenty to fifty per cent. in the deposits and scale of marine boilers filled with fresh water, any loss being made up from the exhaust or from sea water has been fully set forth by Lewes,[1] who also gives the causes thereof and remedies therefor. He also alludes to the possibilities of this type of scale forming in stationary boilers.

The specimens presented serve to illustrate the importance of critically examining the nature of the "*organic matter*" of incrustations, the statement "loss of ignition" being far too general.

[CONTRIBUTED FROM THE LABORATORY OF THE LOUISIANA EXPERIMENT STATION AND SUGAR SCHOOL.]

OCCURRENCE OF THE AMINES IN THE JUICE OF SUGAR CANE.

BY J. L. BEESON.

Received June 15, 1896.

THE presence of amines in the products of the sugar beet has long been known, but until this sugar season they have not been known to exist in the juices of sugar cane. Last December, while working with the precipitate formed by the addition of lime water to cane juice, it was noticed that the product dried at about 110° C. had a fishy odor. Upon heating some of this in a test tube over a burner, an alkaline vapor was given off which had a fishy ammoniacal odor. So about 300 grams of the dried substance was gradually heated in a hard glass retort upon a sand bath until an almost complete destructive distillation was effected. The products evolved were passed through a condenser and then through a series of U tubes, each of which was kept at a temperature a little below the boiling-points of each of the principal amines. A solid collected in the condenser tube, and an illuminating gas escaped from the last U tube, which was kept at —10° C. These products were not examined. There collected in the first receptacle about twenty cc. of an acid liquid. This was made alkaline with caustic soda and distilled. The products as before were passed through the series of tubes maintained at the different temperatures, when there

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[1] *Chem. News*, 63, 181.

collected in the first, along with some water, about five cc. of clear liquid, which was strongly alkaline, had a pungent fishy odor, combined with hydrochloric acid, and otherwise manifested the general properties of the amines. An attempt was made to further purify it by freeing it from the water, but the amount was too small to bring to a definite boiling-point. The remaining liquid was neutralized with hydrochloric acid, and slowly evaporated down, whereupon a few crystals, slightly colored and deliquescent, were obtained. The quantity was too small to admit of an elementary analysis, so it was not possible to say whether the product was a single amine or a mixture of amines. The filter cake, the refuse from the clarification of cane juice, gave the same odor and alkaline vapor upon heating. It was my aim to subject several pounds of the filter cake to the same treatment in order to fully clear up the question, if possible, but the amount of other work required of me prevented. The clearing up of the matter is of the greatest scientific and practical interest to the sugar industry, as it will doubtless throw light upon the nature both of the amido and albuminous bodies of the cane juice. I write the account of the work with the hope that some chemist may be induced to continue the work, as the writer will discontinue sugar work.

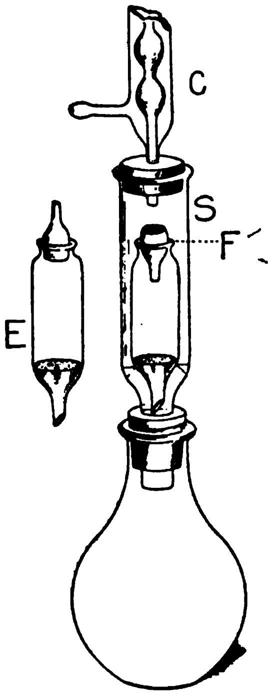
[CONTRIBUTED FROM THE LABORATORY OF THE LOUISIANA EXPERIMENT STATION AND SUGAR SCHOOL.]

A SIMPLE AND CONVENIENT EXTRACTION APPARATUS FOR FOOD-STUFF ANALYSIS.

BY J. L. BEESON.

Received June 15, 1896.

THE apparatus shown in the accompanying illustration I have adapted from the Johnston extractor, for the general use of the average student in the laboratory aiming at simplicity, greater compactness, convenience, rapidity of operation, and accuracy. The extraction tube *E*, which is rather short, is provided as usual with a perforated platinum disk fused into the bottom, and in addition with a specially devised funnel stopper of ground glass, by means of which the weighed sample can be rapidly and effectively dried to constant weight in a current of dry hydrogen or other inactive gas for the estimation of the moisture, and at the same time preparing the sample for extraction. Rubber caps are placed over the two ends of the tube during the cooling and weighing. For the extraction of the sample, the tube *E* is placed in a Stutzer tube *S* as shown in the figure, which is connected as usual with an ether flask below, and by means of either a cork or mercury joint with a short bulb condenser above. The funnel stopper, placed as shown, directs the returning drops of the liquid upon the center of the sample, and especially it prevents the loss of the sample by spattering. This is a source of objection to all forms of open extractors. Owing to the very small percentage of fats or ether extracts in most food stuffs a small loss of the sample from this cause makes a very large analytical error in the work, whether estimated from loss of the sample or gain in weight of the ether flask. During two years use in this laboratory we have obtained with the apparatus very concordant results between duplicate analyses, and would commend it for the use of students especially. By means of a seven mm. glass tube, six tubes and samples are dried in a current of hydrogen at a time in a water-oven. The whole apparatus may be had of Max Kaehler and Martini, Berlin.



NEW BOOKS.

Chemistry for Engineers and Manufacturers. By Bertram Blount and A. G. Bloxam. In two volumes. Volume I, Chemistry of Engineering, Building and Metallurgy. 8vo. 244 pp. London: Charles Griffin & Co., Ltd. Philadelphia: J. B. Lippincott Co.

This work is a compilation of material intended to cover the chief branches of chemical industry. The first volume deals in the first part with the chemistry of building materials, fuel, steam making and lubrication. The second part is entirely devoted to metallurgy.

The scope of the work necessitates condensation, yet the reader will be impressed at times with the meagerness of description, especially as the treatment of other subjects seems disproportionately extended. An appearance of unevenness in treatment is thus given, which might have been avoided.

Books of this class are more difficult to write as the limits of technical science are widened and there is room for much judgment in holding a proper balance between the necessities of the reader and the restricted space of a hand book or text book. While this book will be very serviceable to the large class of engineers and manufacturers for whom it is especially written, and even to the student of industrial chemistry, it can hardly be of much interest to " the expert in any one of the branches touched upon" (*vide* preface). The touch is entirely too light as a rule for those who seek extended information. The entire absence of references, also, deprives the work of much of the usefulness it might have had for professional readers in subjects not strictly their own.

The illustrations are good as far as they go, but are much less freely supplied than the nature of the book requires.

The subjects of gaseous fuel and water for steam making are well and clearly treated. Of boiler compositions the authors justly say that " none should be used without a knowledge both of its composition and of that of the water to be treated," and that, " all are sold at prices bearing but a remote relation to their intrinsic values." As to the preservation of iron by paint, the statement that red lead paint is the best will hardly meet unqualified assent.

The treatment of the metallurgy of iron is very full, and contains a good though brief discussion of the influence of foreign elements on the quality of iron. The statement that "the chief gold-producing countries are Australia, America (California), and Russia" is more compact than edifying. Electrometallurgical processes are given in treating of many of the metals. The commercial production of aluminum is described briefly but no allusion is made to the part which the United States have played in the development of this industry, nor do the names of Cowles or Hall appear in the text.

The second volume will treat of the chief chemical industries other than those referred to.

A. A. BRENEMAN.

LABORATORY EXPERIMENTS IN GENERAL CHEMISTRY. BY CHARLES R. SANGER, A.M., PH.D. Paper. St. Louis. Published by the Author. 1896.

EXPERIMENTS IN GENERAL CHEMISTRY AND QUALITATIVE ANALYSIS. BY CHARLES R. SANGER, A.M., PH.D. Paper. St. Louis. Published by the Author. 1896.

These two little books by Professor Sanger contain well selected collections of experiments for beginners in chemistry. The first collection was prepared for students in a general college course, while the second collection appears to have been arranged for students beginning a medical course. In the first collection for college students there is evidence that the author had in mind the needs of those who spend but part of a year in the laboratory. What the student is told to do is clearly indicated and his attention is directed at every step to the important points in the reactions considered. The experimental course offered to medical students is not as extended as the present writer would like to see, but is as full as this class of students is supposed to need, and has, besides, the advantage of systematic arrangement.

J. H. LONG.

BOOKS RECEIVED.

Eighth Annual Report of the Kentucky Agricultural Experiment Station of the State College of Kentucky, for the year 1895. Lexington, Ky. lxvi, 150 pp.

North Carolina Weather during the Year 1895. North Carolina Agricultural Experiment Station, Raleigh, N. C. lii, 264 pp.

Bulletin No. 122. Cost of Nitrogen, Phosphoric Acid and Potash. Proper Use of Tables of Analysis of Fertilizers. Connecticut Agricultural Experiment Station, New Haven, Conn. 16 pp.

Reduction of Nitrates by Bacteria and Consequent Loss of Nitrogen. By Ellen H. Richards and George William Rolfe. 20 pp. Reprinted from the *Technology Quarterly*, Vol. IX, No. 1, March, 1896.

Nitro-Explosives. A Practical Treatise. By P. Gerald Sanford, F. I. C.,

F. C. S. London: Crosby, Lockwood & Son. 1896. xii, 270 pp. Price, 9s.

Embalming and Embalming Fluids, with the Bibliography of Embalming. Thesis by Charles W. McCurdy, Sc.D., Ph.D. Wooster, Ohio: The Herald Publishing Co. April, 1896. 84 pp.

Bulletin No. 64. Analysis of Commercial Fertilizers. Kentucky Agricultural Experiment Station of the State of Kentucky, Lexington, Ky. July, 1896. 16 pp.

OBITUARY NOTE.

Peter Collier, Ph.D., was born in Chittenango, New York, August 17, 1835. He graduated A.B. at Yale College in 1861 and later Ph.D. He also graduated at the Sheffield Scientific School, and was for some time an assistant and instructor in that School. From 1867 to 1877, he was Professor of Physics and Chemistry in the University of Vermont, and also Professor of Chemistry in the Medical Department of that University, and for some time Dean of the Medical Faculty. In 1873 he was appointed one of seven scientific commissioners to the Vienna Exposition, by President Grant. From 1877 to 1882 he was Chief Chemist to the Department of Agriculture of the United States, at Washington. During his official term, he gave very great attention to the problems of cultivating sorghum and manufacturing sugar from it. From 1882 to 1885 he still remained in Washington, engaged in chemical pursuits and writing for scientific and agricultural publications. From 1887 to 1895 he was Director of the New York State Experiment Station at Geneva, New York, where he instituted much experimental work especially upon fertilizers and dairy problems. He had a wide acquaintance with scientific men, and himself possessed great energy and force. Illness obliged him to resign his position last year and he came to Ann Arbor last December. He died on June 29.

A. B. Prescott.

ERRATA.

On page 651, July number, 15th line from top, for 159,000 *read* 166,000.
On page 653, 7th line from bottom, for 159 000 *read* 166,000.
On page 654, 4th line from top, for 136,519.5 *read* 116,519.5.

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THE DETERMINATION OF REDUCING SUGARS IN TERMS OF CUPRIC OXIDE.

BY GEORGE DEFREN.

Received July 9, 1896.

IT is now approximately fifty years since alkaline metallic solutions were first used in determining quantitatively the various reducing sugars. During this period of time many investigators have worked on the subject, and much has been done towards perfecting the method of analysis, so that to-day there are several admirable processes in use for the exact estimation of these carbohydrates.

The quantitative methods of determining reducing sugars may be divided into two main classes: those based upon the volumetric plan, and those which depend on a gravimetric estimation of the precipitated cuprous oxide.

Of the first class many processes have been suggested which have met with more or less success. The volumetric methods are mainly used for factory control work, where the progress of some processes require a rapid and fairly accurate idea of the stage of manufacture. In expert hands the volumetric methods are capable of giving excellent and concordant results, and are, therefore, used in the laboratories of many consulting chemists, and even in scientific institutions.

The main objections to the use of the volumetric methods are that each freshly prepared quantity of Fehling solution requires accurate standardization against the same kind of pure sugar as that which is undergoing analysis. Different dilutions and the time of boiling affect the results materially. The exact determination of the "end point" also requires considerable practice and skill.

On the other hand, the Fehling liquor used in the gravimetric processes need not be made up as accurately as is required for volumetric work. The gravimetric methods, however, ordinarily require more time. A possible loss of cuprous oxide by filtration, and an incomplete oxidation to the higher oxide are also potent factors, though where the requisite degree of care is exercised these need not cause anxiety. The same statement regarding dilution and time of boiling holds true with as much force in gravimetric as in volumetric work.

The gravimetric methods are generally employed for scientific and accurate analytical work. Here the processes are comparatively few, all depending upon the oxidation of the total sugar present in an excess of the alkaline copper solution.

The tables in use for the determination of reducing sugars are mainly constructed in terms of metallic copper. As the amount of metal precipitated per gram of carbohydrate is not a constant for all dilutions of any sugar, specially constructed tables are generally employed. Several such tables have been prepared, as for instance Allihn's table of reduced copper for dextrose, Wein's table for maltose, and Soxhlet's table for lactose, etc.

Various modifications of the alkaline copper solutions are used for the determination of the different sugars, each requiring special treatment. Therefore a chemist in determining the amount of malt sugar in, say beer, must, if he uses Wein's table for maltose, follow exactly Wein's method for the estimation of that sugar.

Where a variety of work is carried on in a laboratory, it is therefore necessary to have several different Fehling solutions on hand for each special kind of determination. If all the tables for the estimation of the different carbohydrates could have been prepared for use under uniform conditions, the existing state of affairs would be much simplified.

In order to supply this need, I have constructed such tables, using a method which I have employed for some time, in determining reducing sugars. This method, proposed by O'Sullivan[1] in 1876, is used to some extent in England, but as it seems to be not generally known, I here give the procedure in detail:

To fifteen cc. of the copper sulphate solution, prepared as given below, are added fifteen cc. of the alkaline tartrate solution, in an Erlenmeyer flask having a capacity of from 250–300 cc. The mixture is diluted with fifty cc. of freshly boiled distilled water and placed in a boiling water bath for five minutes. Twenty to twenty-five cc. accurately measured from a calibrated burette of an approximately one-half per cent. solution of the sugar to be analyzed, are then run into the hot Fehling liquor and the whole kept in the boiling water bath for from twelve to fifteen minutes. The flask is then removed from the bath and the precipitated cuprous oxide is filtered as rapidly as possible, either through filter paper or asbestos in a Soxhlet's tube or porcelain Gooch crucible, and washed with boiling distilled water until the wash water no longer reacts alkaline. It is ignited and weighed as cupric oxide as described below. The corresponding amounts of dextrose, maltose or lactose are ascertained by reference to the tables at the end of this article. It should be noted that the above directions must be closely followed. The volume of the Fehling liquor and the added sugar solution should be from 100–105 cc.

The Fehling solution used is made up according to Soxhlet's formula, with a very slight modification. 69.278 grams of pure crystallized copper sulphate, pulverized and dried between filter paper, are dissolved in distilled water. It is advantageous to add one cc. of strong sulphuric acid to this, as recommended by Sutton.[2] The whole is then made up to one liter with distilled water and kept in a separate bottle. The alkaline tartrate solution is made by dissolving 356 grams of crystalline Rochelle salt and 100 grams of sodium hydroxide in distilled water and making up to one liter. This is also kept in a separate bottle.

Two methods of filtration of the precipitated cuprous oxide and further treatment are generally adopted. In the first double "washed" filter paper is used; in the other the precipitate is

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[1] *J. Chem. Soc.*, **2**, 130, *1876*.

[2] Sutton: Fourth edition, (1882), 256.

retained by a layer of asbestos. After washing the precipitate on the filter paper as above described, it is dried in the usual manner and ignited in a previously weighed porcelain crucible, taking care to burn the filter paper cautiously, heating for fifteen minutes to a red heat, cooling the crucible over sulphuric acid in a desiccator and weighing as cupric oxide. Additional treatment with nitric acid has been found of no practical advantage, the results by direct ignition being very exact, providing the filter paper is slowly burned. The chief objection to the employment of filter paper to retain the precipitated cuprous oxide, is that some of the finely divided particles are liable to go through, thus causing low results.

As a substitute for paper carefully selected asbestos is often used for filtering purposes. To insure a layer of asbestos which shall be kept at constant weight under the action of hot Fehling liquor, it is advantageous to boil the mineral with nitric acid (1.05–1.10 sp. gr.) for a short time, washing the acid out with hot water, and then boiling with a twenty-five per cent. solution of sodium hydroxide. This is also washed out with hot water. Reboiling with the above reagents as before diminishes the liability of leaving any soluble portions. As thus prepared the filtering material may be kept indefinitely under water in a wide-mouthed bottle ready for use.

The objections of some chemists[1] to the employment of asbestos on the ground that it loses weight on using, does not seem to hold, when it is prepared as above. A sample boiled as stated with acid and alkali three times, lost only two-tenths milligram when two "blanks" of hot dilute Fehling solution, as used in the process above described, were passed through the mineral in a porcelain Gooch crucible.

For use, a layer of asbestos, about one centimeter in thickness, is placed in a porcelain Gooch crucible, to retain the finely divided precipitate, which is filtered by means of suction, in the usual manner. The crucible containing the cuprous oxide is then dropped into a triangular frame, made of platinum wire, suspended within an iron radiator, or shell, heated to redness. This quickly and thoroughly dries the asbestos without cracking

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[1] K[illegible] *Ztschr. angew. Chem.*, 43[illegible] [illegible] Praeger, *Ztschr. angew. Chem.*, 530, *1894*.

the crucible. After about five minutes the crucible is transferred by means of a pair of nippers to a red hot platinum crucible and heated for about fifteen minutes. It is then quickly transferred to a desiccator near at hand to prevent cracking, allowed to cool and weighed. As cupric oxide is somewhat hygroscopic, it is advantageous to weigh quickly and to keep the balance case as dry as possible. Prolonged heating in the iron radiator would have changed the cuprous oxide to the cupric state. The advantage of transferring the porcelain crucible to a red-hot platinum crucible, is that the oxidation is quickly completed, as a much higher temperature is available.

If pressed for time, another determination can be made in the same crucible without cleaning it. As a rule, it is, however, advisable to wash out the cupric oxide by means of hot nitric acid (1.05–1.10 sp. gr.) and then with hot water. The crucible is then heated, cooled and weighed as before. It must necessarily be weighed, because this treatment with hot nitric acid dissolves some of the asbestos.

If preferred, a Soxhlet's tube may be used to retain the precipitated cuprous oxide. As a porcelain Gooch crucible possessed obvious advantages over this apparatus, I have used it in all my determinations with success.

The cupric reducing powers of dextrose, maltose aud lactose were determined by the method given above. A table for invert sugar was not constructed because most invert sugar determinations are made by double polarization in a saccharimeter.

DEXTROSE.

The "cupric reducing power" of dextrose was first determined. This is defined as "the amount of cupric oxide which 100 parts reduce."[1] This may be represented by $\frac{100\,W}{D}$, in which W is the weight of cupric oxide obtained by the given weight of any sugar, and D the weight of cupric oxide formed by an equal weight of dextrose.[2] Hence, if the amount of cupric oxide formed by one gram of dextrose be known, the amount of cupric oxide reduced by one gram of any other substance, calculated

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[1] *J. Chem. Soc.*, 2, 130, *1876*.

[2] *J. Chem. Soc.*, *Trans.*, 606, *1879*.

upon this number as a percentage, will represent the cupric oxide reducing power of the substance, which we denote by the symbol K.

The amount of cupric oxide has been determined by O'Sullivan[1] to be 2.205 grams per gram dextrose. The factor for dextrose in terms of cupric oxide is, therefore, the reciprocal of 2.205 or 0.4535. This value, 0.4535, was assumed to be a constant for all amounts of dextrose when used with Fehling's solution in the manner indicated. As such it was a very convenient quantity, it being only necessary to obtain the weight of cupric oxide formed by the action of a dextrose solution, multiply this by 0.4535, and the amount of dextrose corresponding was obtained. No tables are needed if this assumption be true. Consequently the determination of dextrose was indeed a very simple one.

On an extended investigation of this subject, using various amounts of dextrose on the same volume of Fehling liquor in each determination, I find that the value 2.205, above given as representing the quantity of cupric oxide obtained by the action of one gram of dextrose, is not as was heretofore assumed, a constant for all weights of dextrose taken, the amount varying from 2.27 grams cupric oxide per gram dextrose for small quantities of sugar, to 2.22 grams cupric oxide for the largest amount of dextrose permissible. Allihn,[2] boiling his sugar solutions with the Fehling liquor and reducing the cuprous oxide to copper, obtained analogous varying results.

The purity of the dextrose used was first determined, dextrose anhydride being employed. 10.008 grams of anhydrous dextrose were disssolved in distilled water and the solution boiled to prevent birotation. It was then transferred to a flask, the capacity of which at 15.5° C. was 100.08 cc., thus giving a solution which contained 0.100 gram dextrose anhydride per cc.

The specific gravity of the above solution at 15.5° was determined in the usual manner by means of a picnometer with thermometer attached.

Capacity picnometer (at 15.5°) = 55.2055 cc.
Dextrose solution (at 15.5°) = 57.3083 grams.

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[1] *Loc. cit.*

[2] *J. prakt. Chem.*, (2), 22, 63.

On calculating from these values we find the specific gravity of a dextrose solution containing ten grams dextrose in 100 cc. to be 1.03809 at 15.5°.

The specific rotatory power was determined by the usual method, a Schmidt and Haensch saccharimeter being used in polarizing the dextrose solution. The polarizations were carried out in a 200 millimeter tube at 20°. To change from the readings of a saccharimeter to the rotary degrees, it is necessary to multiply the reading observed by 0.344, as shown by Reinbach.[1] I have verified this value with concordant results, a Laurent polariscope being used for comparison. The rotation of the above solution was 30.7 divisions. This gives by means of the usual formula — $[\alpha]_D^{20} = \frac{\alpha v}{lw}$ — a specific rotatory power of 52.8°, which is in accordance with that obtained by other observers.[2] The dextrose used was consequently pure.

For the determination with Fehling liquor, twenty-five cc. of the dextrose solution at 15.5° were accurately measured from a calibrated burette and made up to 500 cc. with distilled water at the same temperature. This consequently gave a solution, each cubic centimeter of which contained five milligrams dextrose. Various quantities of this were then taken to ascertain the cupric reducing power of dextrose. The results in detail are given below. In each case the combined volumes of the Fehling liquor and the sugar solution were made up to 105 cc. as described above.

Milligrams dextrose.	Cupric oxide obtained.	Cupric oxide per gram dextrose.	Dextrose equivalent.	Mean dextrose equivalent.
12½	0.0283	2.264	0.4416	0.4401
12½	0.0285	2.280	0.4386	
25	0.0569	2.276	0.4393	0.4419
25	0.0565	2.260	0.4425	
50	0.1129	2.258	0.4429	0.4440
50	0.1123	2.246	0.4452	
62½	0.1407	2.251	0.4443	0.4449
62½	0.1403	2.245	0.4454	
75	0.1683	2.244	0.4457	0.4462
75	0.1679	2.239	0.4467	

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[1] *Ber. d. chem. Ges.*, 27, 2282.

[2] Pribram: *Monat. f. Chem.*, 9, 399; Landolt: *Ber. d. chem. Ges.*, 21, 191.

Milligrams dextrose.	Cupric oxide obtained.	Cupric oxide per gram dextrose.	Dextrose equivalent.	Mean dextrose equivalent.
100	0.2233	2.233	0.4478	0.4483
100	0.2227	2.227	0.4489	
125	0.2776	2.221	0.4503	0.4503
125	0.2782	2.225	0.4493	
125	0.2770	2.216	0.4512	
125	0.2774	2.219	0.4506	
125	0.2777	2.222	0.4500	
140	0.3105	2.218	0.4508	0.4511
140	0.3100	2.215	0.4515	

The foregoing values of the amounts of cupric oxide per gram dextrose are given graphically in curve *A*, Plot I, and the dextrose equivalents of this in *A*, Plot II.

From this we get the amount of dextrose corresponding to a given weight of copper oxide by means of the formula:

$$D = (0.4400 + 0.000037\ W)\ W,$$

in which D is the amount of dextrose, and W the weight of cupric oxide.

The dextrose table given in this article is based on this formula, the values of W varying from 30 to 320.

MALTOSE.

The cupric reducing power of dextrose is given as 100. Using this as a basis, the reducing force of maltose, as given by O'Sullivan,[1] is 65. Brown and Heron[2] place the value somewhat lower, claiming that 61 is more exact. The results which I have obtained agree very well with this latter number.

In the case of maltose, as with dextrose, it was found that the amount of cupric oxide obtained per gram of sugar was not a constant. The cupric reducing power of various amounts of maltose was, however, found to be almost exactly a constant when referred to the cupric oxide from equal weights of dextrose. That is, calling the reducing power of dextrose 100 for different aliquot parts of that sugar, the cupric reducing power of maltose referred to this standard was always 61.

The specific gravity of maltose was determined in the usual manner. 9.7558 grams maltose anhydride were dissolved in distilled water to 100.08 cc. at 15.5°.

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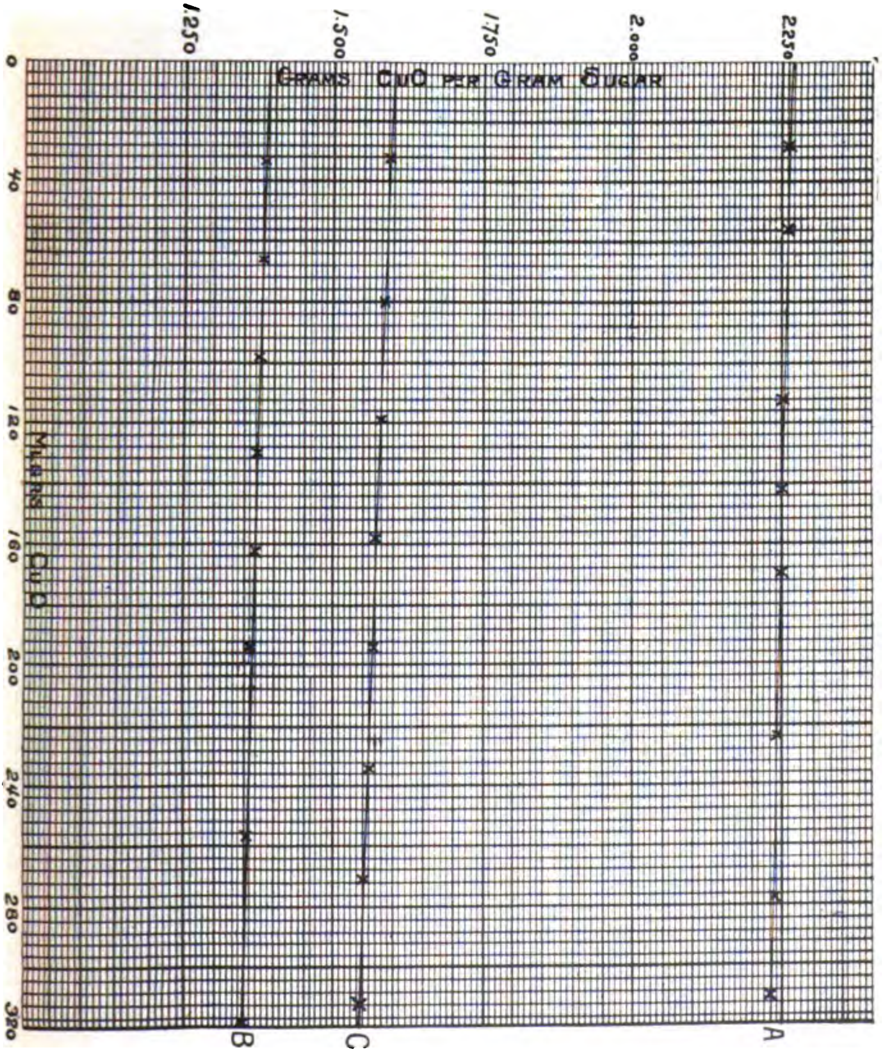
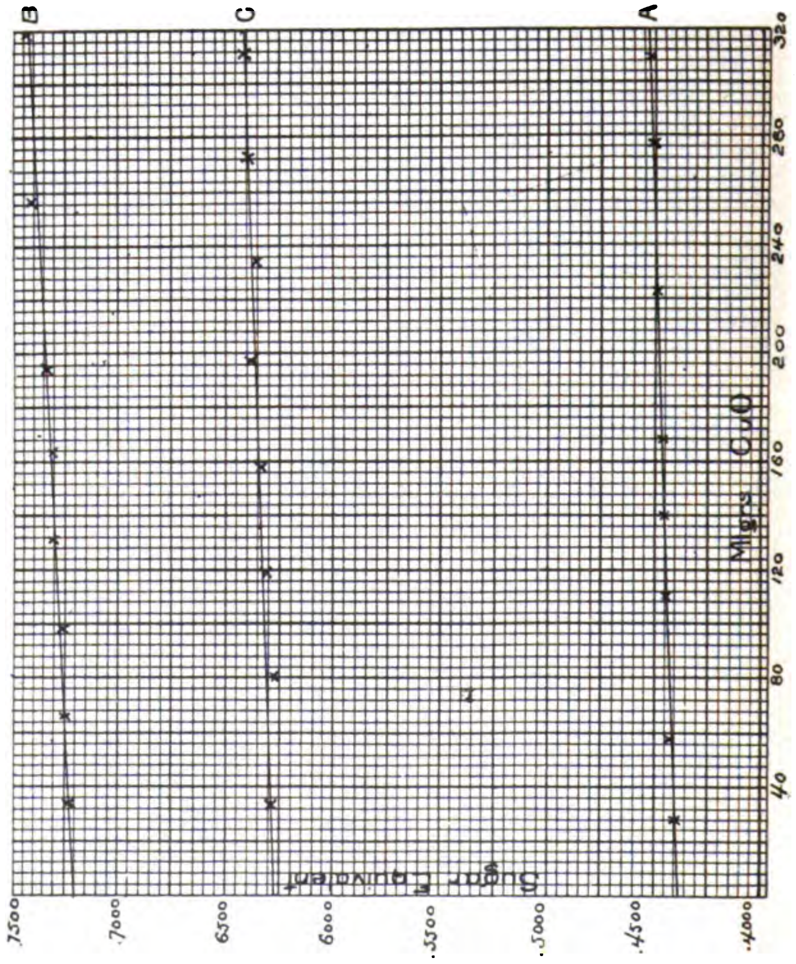
[1] *Loc. cit.*

[2] *J. Chem. Soc.*, *1879*, Trans., 619.


1.250
1.500
1.750
2.000
2.250
Grams CuO per Gram Sugar
0
40
80
120
160
200
240
280
320
Mlgrs CuO
B
C
A

Plot 1.


B
C
A
Mlgrs CuO
40
80
120
160
200
240
280
320
Sugar Equivalent
7500
7000
6500
6000
5500
5000
4500
4000

Plot 2.

Maltose solution at 15.5° = 57.3049 grams.

On calculating this we find the specific gravity of the above solution to be 1.03803. For a solution containing ten grams maltose anhydride in 100 cc. it would consequently be 1.03900 at 15.5°.

The specific rotatory power was determined as usual. The rotation of the above solution at 20°, in a 200 millimeter tube, was 74.4 divisions on the saccharimeter scale. This gives $[\alpha]_D^{20} =$ 136.6°.

As maltose anhydride is somewhat difficult to prepare, the solutions used to determine the cupric reducing powers were made up to approximately ten per cent. from the maltose hydrate. The specific gravity of the solutions was then determined. Subtracting from this value 1.00000—the specific gravity of water—and dividing the remainder by 0.00390, we get the amount of maltose anhydride in 100 cc. of solution.

Maltose solution at 15.5° = 57.2511 grams,

which gives a specific gravity of 1.03754, or 9.501 grams maltose anhydride in 100 cc.

The solution for Fehling determinations was made in the same manner as the dextrose solutions above. Each cubic centimeter of the diluted maltose solution therefore contained 4.75 milligrams maltose anhydride.

Milligrams maltose.	Cupric oxide obtained.	Cupric oxide per gram maltose.	Maltose equivalent.	Mean maltose equivalent.
23.75	0.0329	1.386	0.7218	0.7240
23.75	0.0327	1.377	0.7263	
47.5	0.0656	1.381	0.7243	0.7253
47.5	0.0654	1.377	0.7263	
71.25	0.0983	1.380	0.7247	0.7263
71.25	0.0979	1.374	0.7278	
95.0	0.1304	1.373	0.7286	0.7297
95.0	0.1300	1.369	0.7308	
118.75	0.1623	1.370	0.7302	0.7319
118.75	0.1619	1.367	0.7336	
142.5	0.1940	1.361	0.7345	0.7354
142.5	0.1934	1.357	0.7369	
190.0	0.2572	1.353	0.7284	0.7395
190.0	0.2566	1.350	0.7406	
237.5	0.3198	1.347	0.7429	0.7433
237.5	0.3193	1.345	0.7437	

The maltose equivalent in terms of copper oxide is shown in *B*, Plot II. From this we get the amount of maltose corresponding to a given weight of cupric oxide by the formula:

$$M = (0.7215 + 0.000061\ W)\,W,$$

in which M is the weight of maltose, and W the amount of cupric oxide obtained. It will be seen that these values make the cupric reducing power of maltose 0.61 that of dextrose.

LACTOSE.

Lactose was investigated in the same manner as the preceding. 10.008 grams lactose anhydride were dissolved in distilled water, boiled, and made up to 100.08 cc. at 15.5°.

The above solution, polarized in a 200 millimeter tube at 20°, gave a rotation of 30.7 divisions. This gives the specific rotary power of lactose of 52.8°.

The amounts of cupric oxide found by the reduction of known weights of lactose were determined as in the previous cases with the following results:

Milligrams lactose.	Cupric oxide obtained.	Cupric oxide per gram lactose.	Lactose equivalents.	Mean lactose equivalents.
20	0.0319	1.595	0.6269	0.6289
20	0.0317	1.585	0.6308	
50	0.0798	1.596	0.6266	0.6274
50	0.0796	1.592	0.6282	
75	0.1188	1.584	0.6313	0.6323
75	0.1184	1.579	0.6334	
100	0.1577	1.577	0.6340	0.6355
100	0.1570	1.570	0.6369	
125	0.1955	1.564	0.6395	0.6379
125	0.1964	1.561	0.6363	
150	0.2345	1.563	0.6397	0.6404
150	0.2340	1.560	0.6410	
175	0.2729	1.560	0.6412	0.6418
175	0.2724	1.557	0.6424	
200	0.3112	1.556	0.6425	0.6430
200	0.3107	1.553	0.6436	

The cupric oxide values per gram lactose are presented graphically in curve *C*, Plot I, while the reciprocals of these quantities are shown in *C*, Plot II. For this latter the amount of lactose corresponding to the weight of cupric oxide obtained is determined by the following:

$$L = (0.6270 + 0.000053\ W)\ W,$$

in which L is the lactose, and W the amount of copper oxide. The acompanying table for lactose is constructed on this basis.

* * * * * * *

It will be seen from the above results that the amount of cupric oxide produced by the action of one gram of reducing carbohydrate on Fehling liquor, in the manner described, is not a constant for all dilutions.

The cupric reducing power of maltose is 0.61 that of dextrose.

The following tables for the determination of the reducing sugars in terms of cupric oxide are based on the analytical results presented above, and can be used in the process outlined in the same manner as any other table for the same purpose:

Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.
30	13.2	21.7	18.8	57	25.1	41.3	35.9
31	13.7	22.4	19.5	58	25.5	42.1	36.5
32	14.1	23.1	20.1	59	26.0	42.8	37.1
33	14.6	23.9	20.7	60	26.4	43.5	37.8
34	15.0	24.6	21.4	61	26.9	44.3	38.4
35	15.4	25.3	22.0	62	27.3	45.0	39.0
36	15.9	26.1	22.6	63	27.8	45.7	39.7
37	16.3	26.8	23.3	64	28.2	46.5	40.3
38	16.8	27.5	23.9	65	28.7	47.2	40.9
39	17.2	28.3	24.5	66	29.1	47.9	41.6
40	17.6	29.0	25.2	67	29.5	48.6	42.2
41	18.1	29.7	25.8	68	30.0	49.4	42.8
42	18.5	30.5	26.4	69	30.4	50.1	43.5
43	19.0	31.2	27.1	70	30.9	50.8	44.1
44	19.4	31.9	27.7	71	31.3	51.6	44.7
45	19.9	32.7	28.3	72	31.8	52.3	45.4
46	20.3	33.4	29.0	73	32.2	53.0	46.0
47	20.7	34.1	29.6	74	32.6	53.8	46.6
48	21.2	34.8	30.2	75	33.1	54.5	47.3
49	21.6	35.5	30.8	76	33.5	55.2	47.9
50	22.1	36.2	31.5	77	34.0	56.0	48.5
51	22.5	37.0	32.1	78	34.4	56.7	49.2
52	23.0	37.7	32.7	79	34.9	57.4	49.8
53	23.4	38.4	33.3	80	35.4	58.1	50.5
54	23.8	39.2	34.0	81	35.9	58.9	51.1
55	24.2	39.9	34.6	82	36.3	59.6	51.7
56	24.7	40.5	35.2	83	36.8	60.3	52.4

Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.
84	37.2	61.1	53.0	127	56.5	92.5	80.4
85	37.7	61.8	53.6	128	56.9	93.3	81.1
86	38.1	62.5	54.3	129	57.3	94.0	81.7
87	38.5	63.3	54.9	130	57.8	94.8	82.4
88	39.0	64.0	55.5	131	58.2	95.5	83.0
89	39.4	64.7	56.2	132	58.7	96.2	83.6
90	39.9	65.5	56.8	133	59.1	97.0	84.2
91	40.3	66.2	57.4	134	59.6	97.7	84.9
92	40.8	66.9	58.1	135	60.0	98.4	85.5
93	41.2	67.7	58.7	136	60.5	99.2	86.1
94	41.7	68.4	59.3	137	60.9	99.9	86.8
95	42.1	69.1	60.0	138	61.3	100.7	87.4
96	42.5	69.9	60.6	139	61.8	101.4	88.1
97	43.0	70.6	61.2	140	62.2	102.1	88.7
98	43.4	71.3	61.9	141	62.7	102.8	89.3
99	43.9	72.1	62.5	142	63.1	103.5	90.0
100	44.4	72.8	63.2	143	63.6	104.3	90.6
101	44.8	73.5	63.8	144	64.0	105.0	91.3
102	45.3	74.3	64.4	145	64.5	105.8	91.9
103	45.7	75.0	65.1	146	64.9	106.5	92.6
104	46.2	75.7	65.7	147	65.4	107.2	93.2
105	46.6	76.5	66.3	148	65.8	108.0	93.9
106	47.0	77.2	67.0	149	66.3	108.7	94.5
107	47.5	77.9	67.6	150	66.8	109.5	95.2
108	48.0	78.7	68.2	151	67.3	110.2	95.8
109	48.4	79.4	68.9	152	67.7	111.0	96.5
110	48.9	80.1	69.5	153	68.3	111.7	97.1
111	49.3	80.9	70.1	154	68.7	112.4	97.8
112	49.8	81.6	70.8	155	69.2	113.2	98.4
113	50.2	82.3	71.4	156	69.6	113.9	99.1
114	50.7	83.1	72.0	157	70.0	114.7	99.7
115	51.1	83.8	72.7	158	70.5	115.4	100.4
116	51.6	84.5	73.3	159	70.9	116.1	101.0
117	52.0	85.2	74.0	160	71.3	116.9	101.7
118	52.4	85.9	74.6	161	71.8	117.6	102.3
119	52.9	86.6	75.2	162	72.3	118.4	103.0
120	53.3	87.4	75.9	163	72.7	119.1	103.6
121	53.8	88.1	76.6	164	73.2	119.9	104.3
122	54.2	88.9	77.2	165	73.6	120.6	104.9
123	54.7	89.6	77.9	166	74.1	121.4	105.6
124	55.1	90.3	78.5	167	74.5	122.1	106.2
125	55.6	91.1	79.1	168	74.9	122.9	106.9
126	56.0	91.8	79.8	169	75.4	123.6	107.5

Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.
170	75.8	124.4	108.2	213	95.3	156.3	136.0
171	76.3	125.1	108.8	214	95.8	157.1	136.7
172	76.8	125.8	109.5	215	96.3	157.8	137.3
173	77.3	126.6	110.1	216	96.7	158.6	138.0
174	77.7	127.3	110.8	217	97.2	159.3	138.6
175	78.2	128.1	111.4	218	97.6	160.0	139.3
176	78.6	128.8	112.0	219	98.1	160.8	139.9
177	79.1	129.5	112.6	220	98.6	161.5	140.6
178	79.5	130.3	113.3	221	99.0	162.3	141.2
179	80.0	131.0	113.9	222	99.5	163.0	141.9
180	80.4	131.8	114.6	223	99.9	163.7	142.5
181	80.8	132.5	115.2	224	100.4	164.5	143.2
182	81.3	133.2	115.8	225	100.9	165.3	143.8
183	81.8	134.0	116.5	226	101.3	166.0	144.5
184	82.2	134.7	117.1	227	101.8	166.8	145.1
185	82.7	135.5	117.8	228	102.2	167.5	145.8
186	83.1	136.2	118.4	229	102.7	168.3	146.4
187	83.5	136.9	119.1	230	103.1	169.1	147.0
188	84.0	137.7	119.7	231	103.6	169.8	147.7
189	84.4	138.4	120.4	232	104.0	170.6	148.3
190	84.9	139.1	121.0	233	104.5	171.3	149.0
191	85.4	139.9	121.7	234	105.0	172.1	149.6
192	85.9	140.6	122.3	235	105.4	172.8	150.3
193	86.3	141.4	123.0	236	105.9	173.6	150.9
194	86.8	142.1	123.6	237	106.3	174.3	151.6
195	87.2	142.8	124.3	238	106.8	175.1	152.2
196	87.7	143.6	124.9	239	107.2	175.8	152.9
197	88.1	144.3	125.6	240	107.7	176.6	153.5
198	88.6	145.1	126.2	241	108.1	177.3	154.2
199	89.0	145.8	126.9	242	108.6	178.1	154.8
200	89.5	146.6	127.5	243	109.0	178.8	155.5
201	89.9	147.3	128.2	244	109.5	179.6	156.1
202	90.4	148.1	128.8	245	109.9	180.3	156.8
203	90.8	148.8	129.5	246	110.4	181.1	157.4
204	91.3	149.6	130.1	247	110.9	181.8	158.1
205	91.7	150.3	130.8	248	111.3	182.6	158.7
206	92.2	151.1	131.5	249	111.8	183.3	159.4
207	92.6	151.8	132.1	250	112.3	184.1	160.0
208	93.1	152.5	132.8	251	112.7	184.8	160.7
209	93.5	153.3	133.4	252	113.2	185.5	161.3
210	94.0	154.1	134.1	253	113.7	186.3	162.0
211	94.4	154.8	134.7	254	114.1	187.1	162.6
212	94.9	155.6	135.4	255	114.6	187.8	163.3

Parts. copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts. copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose
256	115.0	188.6	163.9	289	130.2	213.6	185.6
257	115.5	189.3	164.6	290	130.6	214.3	186.2
258	116.0	190.1	165.2	291	131.1	215.1	186.9
259	116.4	190.8	165.9	292	131.5	215.9	187.6
260	116.9	191.6	166.5	293	132.0	216.6	188.2
261	117.3	192.4	167.2	294	132.5	217.4	188.9
262	117.8	193.1	167.8	295	133.0	218.2	189.5
263	118.3	193.9	168.5	296	133.4	218.9	190.2
264	118.7	194.6	169.1	297	133.9	219.7	190.8
265	119.2	195.4	169.8	298	134.3	220.4	191.5
266	119.6	196.1	170.4	299	134.8	221.2	192.1
267	120.1	196.9	171.1	300	135.3	221.9	192.8
268	120.6	197.7	171.7	301	135.7	222.7	193.4
269	121.0	198.4	172.4	302	136.2	223.5	194.1
270	121.4	199.2	173.0	303	136.6	224.2	194.7
271	121.9	199.9	173.7	304	137.1	225.0	195.3
272	122.4	200.7	174.4	305	137.6	225.8	196.0
273	122.8	201.5	175.0	306	138.0	226.5	196.6
274	123.3	202.2	175.7	307	138.5	227.3	197.3
275	123.7	203.0	176.3	308	138.9	228.1	197.9
276	124.2	203.7	177.0	309	139.4	228.8	198.6
277	124.6	204.5	177.6	310	139.9	229.6	199.3
278	125.1	205.2	178.3	311	140.3	230.4	199.9
279	125.6	206.0	178.9	312	140.8	231.1	200.6
280	126.1	206.8	179.6	313	141.2	231.9	201.3
281	126.5	207.5	180.2	314	141.7	232.7	202.0
282	127.0	208.3	180.9	315	142.2	233.4	202.6
283	127.4	209.0	181.5	316	142.6	234.2	203.3
284	127.9	209.8	182.2	317	143.1	234.9	203.9
285	128.3	210.5	182.9	318	143.6	235.7	204.6
286	128.8	211.3	183.6	319	144.0	236.5	205.3
287	129.3	212.1	184.2	320	144.5	237.2	205.9
288	129.7	212.8	184.9				

SUPPLEMENTARY TABLE FOR GLUCOSE ANALYSIS.

The amounts of cupric oxide given above are those obtained by the use of absolute weights of sugar. The tables are constructed on this basis. In the case of a mixed product, like commercial glucose, which may be considered made up of the simple bodies, dextrin, maltose, and dextrose, it is far more convenient to determine the total carbohydrates present in solution by means of the specific gravity than by drying the glucose and obtaining in this way the total solids. For this purpose an arbitrary value is taken which shall represent the influence of one gram of a mixture of the three substances above mentioned on the specific gravity if dissolved to 100 cc. in distilled water. Brown and Heron[1] claim that this influence on the specific gravity of one gram starch conversion product in 100 cc. is 0.00386. This value has been determined to be correct for solutions of cane sugar, and is much used for glucose work.

As above mentioned the specific gravity of a dextrose solution containing ten grams dextrose anhydride in 100 cc. is 1.03809 at 15.5°. To determine the cupric reducing power of a substance using the value 3.86 as a divisor, it therefore becomes necessary to change the figures given in the tables to conform to this new factor, that is, the dextrose equivalents must be multiplied by $\frac{386}{381}$, which has been done for convenience of reference in the following table:

Copper oxide obtained.	Dextrose equivalent.	Copper oxide obtained.	Dextrose equivalent.	Copper oxide obtained.	Dextrose equivalent.
5	0·4461	110	0·4500	215	0·4540
10	0·4463	115	0·4502	220	0·4542
15	0·4465	120	0·4504	225	0·4543
20	0·4467	125	0·4506	230	0·4545
25	0·4468	130	0·4508	235	0·4547
30	0·4470	135	0·4510	240	0·4549
35	0·4472	140	0·4512	245	0·4551
40	0·4474	145	0·4513	250	0·4553
45	0·4476	150	0·4515	255	0·4555
50	0·4478	155	0·4517	260	0·4557
55	0·4480	160	0·4519	265	0·4558
60	0·4482	165	0·4521	270	0·4560
65	0·4484	170	0·4523	275	0·4562
70	0·4485	175	0·4525	280	0·4564
75	0·4487	180	0·4527	285	0·4566
80	0·4489	185	0·4528	290	0·4568
85	0·4491	190	0 4530	295	0·4570
90	0·4493	195	0·4532	300	0·4572
95	0·4495	200	0·4534	305	0·4574
100	0·4497	205	0·4536	310	0.4576
105	0·4498	210	0·4538	315	0·4578
				320	0·4580

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[1] *Loc. cit.*

Thus a solution containing 100 milligrams of mixed carbohydrates, using the factor 0.00386, if it formed 200 milligrams cupric oxide by reduction of the Fehling solution in the manner above described, would have a cupric reducing power, or $K_{3.86}$ of 90.68.

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ALUMINUM ANALYSIS.

By James Otis Handy.

Received June 30, 1896.

ALTHOUGH the aluminum industry is not a large one in the sense that the iron industry is, it is growing very rapidly. The output of the United States in 1894 was 550,000 pounds, and in 1895 it was about 850,000 pounds. The Pittsburg Reduction Company, with works at New Kensington, near Pittsburg, Pa., and at Niagara Falls, N. Y., is the only American producer of aluminum. The material is made by the electrolysis, in carbon-lined pots, of alumina dissolved in a fused bath of fluorides. The product of each pot is ladled out at intervals and is graded according to the analyses of the Pittsburgh Testing Laboratory, Limited. Some of the aluminum is sold as it is made and some is alloyed to modify its physical properties. Alloys of aluminum with three per cent. nickel, or with three to seven per cent. copper, or similar amounts of zinc are very useful on account of increased strength with only slightly increased specific gravity. The aluminum at present produced with the best ores available contains from

99 to 99.9 per cent. of aluminum.
0.3 to 0.05 per cent. of silicon (combined and graphitic).
0.50 to [illegible] per cent. of copper.
0.20 to [illegible] per cent. of iron.
Carbon is sometimes present in aluminum.

Second grade aluminum contains ninety-six to ninety-eight per cent. aluminum, silicon and iron making up the remainder. Aside from analyses of metallic aluminum there are required in the practice of the aluminum industry, analyses of alloys of copper, nickel, manganese, chromium, tungsten, zinc, and titanium, with aluminum ; aluminum solders, containing tin, zinc, and phosphorus ; aluminum hydrate, bauxite, and electrode carbons ; hydrofluoric acid and fluorides.

ANALYSIS OF COMMERCIAL ALUMINUM. (95 to 99.9 PER CENT. PURE).

In the analysis of aluminum we are offered a choice of solvents.

Solubility of Aluminum : Hydrochloric acid of thirty-three per cent., (*i. e.*, one part of hydrochloric acid of 1.2 sp. gr. to two parts water) is a rapid solvent.

Sulphuric acid of twenty-five per cent. dissolves aluminum completely on long boiling.

Nitric acid of one and two-tenths specific gravity dissolves aluminum on prolonged boiling.

Acid mixture : A mixture of the three acids which we term "Acid Mixture" is made of

100 cc. nitric acid of 1.42 sp. gr.
300 cc. hydrochloric acid of 1.20 sp. gr.
600 cc. sulphuric acid of twenty-five per cent.

It is a very useful solvent for aluminum because it supplies oxidizing conditions during solution and so prevents loss of combined silicon as hydride. The sulphuric acid content of the acid mixture furnishes a means of rapidly dehydrating the silica.

Sodium hydroxide solution of thirty-three per cent. is a useful solvent when it is desired to separate the metallic impurities from the bulk of the aluminum at once. Weaker solutions do not work as quickly or completely. Solution succeeds best in an Erlenmeyer flask.

Fifteen cc. of the sodium hydroxide solution suffice for one gram of aluminum.

Commercial soda lye may be used if dissolved and filtered through asbestos.

OTHER REAGENTS AND STANDARD SOLUTIONS USED IN ALUMINUM ANALYSIS.

Sodium carbonate, chemically pure.

Soda ash : "Solvay" soda ash, a saturated solution in water, filtered.

Powdered zinc: Practically free from iron and copper.

Fifteen per cent. nitric wash: (Fifteen parts 1.42 nitric acid to eighty-five parts water).

Standard potassium permanganate: 5.76 grams in two liters. One cc. equals 0.005 grams iron.

Standard potassium cyanide: Forty-five grams in two liters. One cc. is made to equal 0.005 gram coppper.

SPECIAL APPARATUS.

Two narrow glass tubes, graduated roughly, one to hold one gram of powdered zinc and the other one gram of chemically pure sodium carbonate.

The evaporating dishes which are used are, preferably, about four and a half inches in diameter, and are covered with five-inch glasses.

The Erlenmeyer flasks are of about twelve ounce capacity and furnished with porcelain crucible covers.

THE METHOD.

Determination of Silicon, Iron, and Copper in Commercial Aluminum.—One gram of aluminum drillings is dissolved in a four and a half inch evaporating dish in thirty cc. of "acid mixture." If the drillings are thin it is best to add only fifteen cc. at first. Placing cold water on the cover glass sometimes prevents loss from too energetic foaming. Solution having been completed by warming slightly, evaporate quickly to strong fumes of sulphuric acid and continue heating for five minutes. Experience will show on what parts of the hot plate these solutions can be evaporated without spattering at the time when aluminum sulphate begins to crystallize out. Remove the dishes from the plate by means of an iron fork, and in a few moments add to the contents of each seventy-five to 100 cc. of water and ten cc. of twenty-five per cent. sulphuric acid, break up the residue in each dish with a short, heavy glass rod, and place the dishes back on the hot plate. Boil until all aluminum sulphate dissolves. Add to each dish one gram of metallic zinc powder, measured. Be careful to pour the zinc into the middle of the liquid. If it touches the sides of the dish it sometimes becomes firmly fixed there. Keep the dish contents at 60° to 70° C. until the zinc has dissolved, leaving the iron reduced and the copper precipitated. Filter and wash well with hot water. Cool, titrate the filtrates with standard potassium permanganate. One cc. equals 0.50 per cent. iron when one gram of aluminum has been used. Placing new receivers under the funnels, treat each residue twice with hot fifteen per cent. nitric acid wash. Wash out with water, and in the solutions thus obtained, titrate the copper with standard potassium cyanide, after adding saturated soda ash solution until the precipitated copper carbonate redissolves. The end point of the titration is very satisfactory. The cyanide solution should be standardized with copper of known purity in about the amount usually found, *viz.*, 0.005 to 0.010 gram. The residue of silicon and silica are burned off in numbered crucibles and each fused with one gram of chemically pure sodium carbonate (measured). The crucible containing the fused mass is placed in fifteen cc. of water in the porcelain dish originally used, and twenty-five cc. of twenty-five per cent. sulphuric acid are added. Solution takes place quickly without separation of silica, and after rinsing out and removing the crucible, the solution is evaporated to five minutes fuming on the hot plate. After cooling add seventy-five to 100 cc. of water and boil to disintegrate the silica. Filter and wash well with water. Burn off and weigh silica and crucible, treat with hydrofluoric acid and a drop of sulphuric acid if impurity is suspected. Evaporate, ignite, and weigh again. Loss equals silica; calculate to silicon.

Determination of Crystalline (*Graphitic*) *Silicon in Aluminum.* —Dissolve one gram of aluminum in thirty cc. of thirty-three per cent. hydrochloric acid (two parts of water to one of hydrochloric acid) in a platinum dish; add about two cc. of hydrofluoric acid, stir, and filter at once through a No. 0 nine cm. filter, contained in a funnel which has been thinly coated with paraffin. Wash with water and burn off in a platinum crucible. Fuse with one gram of sodium carbonate, cool in fifteen cc. of water in a four and a half inch evaporating dish. Add twenty cc. of twenty-five per cent. sulphuric acid. Rinse out the crucible. Evaporate to fumes, cool, add seventy-five cc. of water, boil up and filter off the silica. Wash, ignite, and weigh. Calculate to silicon.

The determinations of silicon, copper, and iron are the every day methods of grading aluminum. It is recognized that sodium and carbon occasionally exist in aluminum, and they are determined by methods described. In certain samples it is desirable to know the approximate percentage of graphitic and combined silicon. These determinations are also described. We determine nitrogen, if present, by a special method.

DETERMINATION OF SODIUM IN ALUMINUM.

One gram of drillings is dissolved in a porcelain evaporating dish in fifty cc. of 1.3 sp. gr. nitric acid and sufficient hydrochloric acid to effect solution. Boil down until all hydrochloric acid has been removed. Rinse the solution into a large platinum dish and evaporate to dryness. Heat over a good Bunsen burner until nitric oxide fumes cease to be evolved. Grind the residue finely. Mix it by grinding with one gram of chemically pure ammonium chloride and eight grams of chemically pure calcium carbonate. Heat the mixture in a large covered platinum crucible. For the first fifteen minutes have a Bunsen burner flame just touching the bottom of the crucible, and for the next forty-five minutes, have the whole crucible heated bright red by a full Bunsen burner flame. Cool, and treat the residue with hot, distilled water until it becomes just friable under pressure. Avoid adding an excess of water beyond that necessary to make the sintered mass just friable. Grind it in a wedgewood mortar and rinse out with hot distilled water. Filter, rejecting the well washed residue, and treat the filtrate at the room temperature with saturated ammonium carbonate solution in slight excess. Stir very thoroughly. The precipitated calcium carbonate is at first flocculent, but on standing for about ten minutes, it becomes crystalline. Filter into a platinum dish; reject the residue and evaporate the solution on the water-bath to dryness. Heat carefully to dull redness to expel ammonium salts. Dissolve the residue in a little water and add a few drops of ammonium carbonate solution. If this produces a precipitate, add sufficient ammonium carbonate solution to precipitate all of the remaining lime. Stir well, wait ten minutes, filter, evaporate to dryness, heat to dull redness, and weigh sodium chloride. Deduct any sodium chloride found in a blank determination, using acids, etc., as above, and finally eight grams of calcium carbonate and one gram of ammonium chloride.

$$NaCl \times 0.39316 = Na.$$

Care should be taken when heating up the residue of sodium chloride, etc., after evaporating on the water-bath. If the platinum dish and contents are heated for a few minutes on sheet asbestos on the hot plate before placing over the lamp, spattering may be avoided. Sodium is generally absent from aluminum, but it has been found in amounts as high as 0.20 per cent. and is considered a cause of the occasional deterioration of the metal in water.

DETERMINATION OF CARBON IN ALUMINUM. (MOISSAN'S METHOD MODIFIED.)

Triturate two grams of drillings in a Wedgewood mortar with ten to fifteen grams of mercuric chloride, powdered and dissolved, or partly dissolved, in about fifteen cc. of water. Reaction takes place rapidly and a heavy gray residue is left. Persistent trituration removes the last particles of metallic aluminum. Evaporate on the water-bath to dryness. The dry residue is heated in a current of pure hydrogen to expel mercuric compounds. The remaining material is then placed in a boat in a combustion tube and burned off as in carbon determination in steel. The carbon dioxide is caught as barium carbonate, and the excess of barium hydroxide determined by means of standard acid. We are working on a more generally applicable method for carbon in aluminum.

DETERMINATION OF NITROGEN IN ALUMINUM.

Aluminum, when overheated in re-melting, is believed to have the property of combining with nitrogen. The metal becomes weaker. Moissan's method for determining nitrogen in aluminum may be found in *Compt. Rend.*, 119, 12. Nitrogen thus absorbed would undoubtedly exist as nitride of aluminum and solution of sodium hydroxide with subsequent distillation would seem to be the best method of procedure. We are working up this method.

DETERMINATION OF ALUMINUM IN METALLIC ALUMINUM.

Dissolve one gram of metal in thirty cc. of thirty-three per cent. hydrochloric acid in a porcelain dish and evaporated cautiously to complete dryness. Redissolve, by boiling, with ten cc. of concentrated hydrochloric acid and seventy-five cc. of water. Wash into a twelve ounce beaker; dilute to 250 cc. and pass hydrogen sulphide until saturated. Filter into a beaker and boil off hydrogen sulphide. Oxidize by adding one cc. of concentrated nitric acid and continuing to boil for ten minutes. Cool and make the solution up to 500 cc. Remove fifty cc. of the solution, and having diluted to 250 cc. and heated to boiling, add ammonium hydroxide in slight excess and boil well for twenty minutes. Let settle; filter, and wash thoroughly with hot water. It is necessary to wash the precipitate off from the filter, break it up, and wash it back again. Finally burn off in a thin-walled platinum crucible, igniting most intensely, and weighing the instant the crucible and content are cool. We have found that alumina is one of the most difficult oxides to dehydrate completely, and when dehydrated it absorbs atmospheric moisture even more rapidly than calcium oxide does. Moissan prefers to precipitate aluminum by ammonium sulphide. Having prepared a solution in hydrochloric acid, he takes an amount equal to 0.15 gram of aluminum, neutralizes it in the cold with ammonia, and precipitates it by ammonium sulphide, which has been recently prepared. He then digests for one hour, filters, washes with hot water, ignites and weighs.

ANALYSIS OF ALLOYS OF ALUMINUM WITH SMALLER AMOUNTS OF OTHER METALS.

Copper Alloys.—Three to thirty per cent. copper, and no zinc or nickel.

Dissolve one-half gram or one gram in fifteen cc. of thirty-three per cent. sodium hydroxide solution in an Erlenmeyer flask of twelve ounce capacity. If the flask is covered and set in a warm place, solution is complete in a few minutes, even if the drillings are quite coarse. Dilute to thirty cc. with hot water and filter through a coarse, lintless filter paper (Whitall, Tatum & Co.'s five inch). Wash well with hot water. Dissolve residue, after washing it off the filter paper into a twelve ounce beaker, by warming with five cc. of concentrated nitric acid. Cool, add saturated commercial sodium carbonate solution until re-solution occurs. Titrate with standard potassium cyanide solution to the disappearance of the blue color. Standardize the cyanide for about the same amount of copper.

For commercial reasons, twenty per cent. alloys are made in the reduction pots, and these alloys are subsequently used for making copper alloys of low percentage.

DETERMINATION OF NICKEL IN ALUMINUM ALLOYS.

The three per cent. nickel alloy is now used. The addition of three per cent. of nickel increases the tensile strength of aluminum by several thousand pounds per square inch.

One gram of drillings is dissolved in fifteen cc. of thirty-three per cent. sodium hydroxide solution in a twelve ounce Erlenmeyer flask. Dilute to fifty cc. and filter through a five-inch lintless paper, washing the residue thoroughly with hot water. Rinse the residue back into the flask and add three to five cc. of concentrated nitric acid, and a drop of concentrated hydrochloric acid. Boïl, and when dissolved, cool, and make up to 250 cc. In 100 cc. determine the copper by neutralizing with ammonia, adding two cc. of concentrated hydrochloric acid, warming and passing hydrogen sulphide. Filter and wash with ammonium sulphide. Burn it off carefully in a porcelain crucible, and having weighed, dissolve in five cc. of concentrated nitric acid. Then dilute to twenty cc., add excess of sodium carbonate solution and titrate with standard potassium cyanide. Boil the filtrate from the cupric sulphide, oxidize with one cc. of nitric acid, and precipitate with ammonium hydroxide. Do not boil, but digest for a few minutes just below the boiling point. Filter, wash, redissolve in hot fifteen per cent. nitric acid wash. Dilute to 150 cc. and again precipitate with excess of ammonium hydroxide, being careful to avoid boiling or prolonged digestion. Filter and wash. Burn off and weigh ferric oxide, etc. In a second

100 cc. of the main solution, precipitate nickel hydroxide, cupric oxide, ferric hydroxide, etc., by thirty-three per cent. chemically pure sodium hydroxide solution, added in slight excess to the boiling solution. Boil for fifteen minutes, filter, and wash most thoroughly with hot water. Burn off and weigh nickel oxide, cupric oxide and ferric oxide. Deduct cupric oxide and ferric oxide already found. Calculate nickel oxide to metallic nickel.

ANALYSIS OF ALUMINUM-MANGANESE ALLOYS.

Determination of Manganese.—Place one gram of drillings in a twelve ounce beaker. Add thirty cc. of thirty-three per cent. hydrochloric acid (one part of concentrated hydrochloric acid to two of water). When dissolved, add twenty-five cc. of nitric acid (1.42), and boil down to ten cc. Add fifty cc. of colorless nitric acid (1.42) and boil. Precipitate the manganese with powdered potassium chlorate, added cautiously, and proceed as described under manganese in steel by Williams' method.[1]

ANALYSIS OF CHROMIUM-ALUMINUM ALLOY.

Determination of Chromium.—Dissolve one gram in a twelve ounce beaker in thirty cc. of thirty-three per cent. hydrochloric acid, and when dissolved add fifty cc. of sulphuric acid (1.84), and evaporate carefully until fumes of sulphur trioxide escape. Cool, add sixty cc. of water and boil. After five minutes, if all aluminum sulphate has been dissolved, add powdered potassium permanganate until the solution has a distinct pink color. Boil until the excess of potassium permanganate is decomposed. Filter through washed asbestos and determine the chromium in the filtrate as in chrome steel.[2]

ANALYSIS OF TUNGSTEN-ALUMINUM ALLOY.

Determination of Tungsten.—Dissolve one gram in thirty-three per cent. hydrochloric acid in a four and a half inch evaporating dish. Add thirty cc. of nitric acid (1.42) and evaporate to dryness. Redissolve in thirty cc. of hydrochloric acid (1.20), dilute to about ninety cc., and boil for two hours. Filter and wash thoroughly. Burn off and weigh Si + SiO_2 + WO_3 + crucible. Treat with three drops of twenty-five per cent. sul-

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[1] Blair's "Chemical Analysis of Iron."

[2] Galbraith's Method. See Blair's "Chemical Analysis of Iron."

phuric acid and about two cc. of hydrochloric acid. Evaporate carefully over an Argand burner, re-ignite, and weigh crucible and silicon and tungstic oxide. Fuse with one gram of sodium carbonate, cool, place in dish, and add fifteen cc. of water and twenty cc. of twenty-five per cent. sulphuric acid, remove crucible and evaporate until white fumes escape. Cool, redissolve in about fifty cc. of water. Filter, wash, ignite, and weigh silica (from silicon), tungstic oxide, and crucible. Treat with sulphuric acid and hydrofluoric acid, evaporate, ignite, and reweigh. Loss equals silica. Calculate to silicon and add to the weight of silica lost by treatment of first insoluble residue. Deduct this sum from the weight of silicon, silica, and tungstic oxide first found and the remainder equals tungstic oxide. Calculate to tungsten.

ANALYSIS OF ALUMINUM-TITANIUM ALLOY.

Determination of Titanium.—Two grams of the alloy in a twelve ounce Erlenmeyer flask are dissolved by addition of fifty cc. of ten per cent. potash solution. Dilute with distilled water to about 125 cc., boil up, and filter as quickly as possible. Wash ten times with boiling water. Burn off the residue in a porcelain crucible, crush it in a Wedgwood mortar, fuse in a large platinum crucible with ten grams of potassium bisulphate. Conduct the fusion exactly as follows: Choose a good Bunsen burner, and protect it from draught by a sheet-iron chimney; make the flame one and a half inches long, and place the triangle carrying the upright crucible just at the point of the flame. Increase the heat gradually until in ten minutes the lower fourth of the crucible is red hot. Allow it to remain at this temperature ten minutes, moving the lid slightly to one side every two minutes, and giving the crucible (held firmly in the tongs) a gentle rotating movement, then turn up the light until the flame reaches the top of the crucible and envelopes it. Five minutes of this treatment melts down any potassium bisulphate, etc., which have risen on the sides. The flame is lowered and the lower fourth heated for ten minutes longer. Cool, dissolve in about 200 cc. of water; filter, rejecting the residue, if ignition and treatment with hydrofluoric acid show it to be only silica.

If it contains anything more, fuse with four grams of potassium bisulphate again. The filtrate contains all the titanic oxide and the ferric oxide. Add ammonia until a slight permanent precipitate is formed, then add dilute sulphuric acid from a pipette or burette until this precipitate just redissolves. Finally add one cc. more of twenty-five per cent. sulphuric acid and dilute to 300 cc. If the solution is high in iron (which will be indicated by its distinct yellow color) sulphur dioxide gas must be run into it until it is decolorized and smells strongly of sulphur dioxide, but if the solution is nearly colorless, indicating a low percentage of iron, only sulphur dioxide water need be added for the reduction. Boil well for one hour, adding water saturated with sulphur dioxide occasionally. Filter off the titanic oxide through double filters and wash well with hot water. Burn off and weigh as titanic oxide. If the precipitate is yellow, indicating the presence of iron, it may be fused with one gram of potassium bisulphate, the fusion dissolved in ten cc. of dilute sulphuric acid, and the iron determined in this solution by reducing with one gram of zinc, and titrating with permanganate. This is not often necessary. Calculate titanic oxide to titanium. $TiO_2 \times 0.6 = Ti$.

DETERMINATION OF ZINC IN ZINC-ALUMINUM ALLOY. FIRST METHOD.

Dissolve one gram in thirty cc. of thirty-three per cent. hydrochloric acid in a twelve ounce beaker. Dilute to 200 cc. and heat nearly to boiling. Pass hydrogen sulphide till all copper is precipitated. Filter and boil off hydrogen sulphide, oxidize with one cc. nitric acid by boiling ten minutes. Add sodium hydroxide solution until neutral, then make barely acid with hydrochloric acid, and stir until the aluminum hydroxide all dissolves. Add ten grams of sodium acetate and 500 cc. of water, boil up, and filter at once. Dissolve the washed precipitate in hydrochloric acid and repeat the acetate separation. Heat the united filtrates to boiling and pass hydrogen sulphide. Filter off the zinc sulphide on double filters, wash thoroughly with hot water. Burn off in a porcelain crucible, and weigh zinc oxide. Calculate to zinc. This method may be used when only a small quantity of the sample is available, but when this is not the case, it is better to use the method given below.

DETERMINATION OF ZINC IN ZINC-ALUMINUM ALLOYS. SECOND METHOD.

Dissolve one gram of drillings in thirty-three per cent. sodium hydroxide solution in a twelve ounce Erlenmeyer flask. Filter as soon as dissolved through a four inch lintless filter paper. Wash thoroughly with hot water. Rinse the residue of zinc, iron, copper, silicon, etc., back into the flask. This may require 25 cc. of water. Add five cc. of hydrochloric acid and boil. Dilute to 150 cc. with hot water and pass hydrogen sulphide. Filter and boil off hydrogen sulphide, reoxidize by adding one cc. nitric acid and boiling ten minutes. Add sodium hydroxide till neutral, then add dilute hydrochloric acid till just acid, and then ten grams of sodium acetate, and 300 cc. of boiling water, and boil for five minutes. Wash well. If the precipitate is small, resolution and reprecipitation are not necessary. Pass hydrogen sulphide through the filtrate. Filter off zinc sulphide through double filters. Wash well. Ignite in a porcelain crucible, heating finally over the blast, to zinc oxide. $ZnO \times 0.8032 = Zn$.

ANALYSIS OF ALUMINUM SOLDERS.

Determination of Tin, Phosphorus, and Zinc.—Aluminum solders generally contain phosphor-tin, and zinc. As presented for analysis, they usually consist of a soldered joint, from which the solder must be scraped and analyzed. The analysis, therefore, involves a separation of the elements aluminum, zinc, tin, and phosphorus. It is a difficult matter to determine whether aluminum was a constituent of the solder when only a soldered joint is available for examination. It is best to dissolve all adhering aluminum from the pieces chosen for analysis by treatment with thirty-three per cent. sodium hydroxide solution after which the residue is filtered off, dried, and weighed out for analysis. Dissolve or decompose three-tenths to five-tenths gram in a twelve-ounce beaker by means of twenty cc. of nitric acid (1.42). If necessary, five cc. of hydrochloric acid (1.2) may be used to effect complete decomposition. Evaporate to complete dryness on a hot plate. Cool, add twenty-five cc. of nitric acid (1.13), and boil thoroughly. Filter. The residue contains all of the tin, most of the phosphorus, and possibly some zinc. Burn it off in a porcelain crucible and, after pulverizing the residue in an agate mortar, mix it with two grams of sodium carbonate and two grams of sulphur, fuse it in a covered porcelain crucible over a Bunsen burner for about half an hour. Give it three minutes of gentle blast flame at the last. Cool, boil out with 150 cc. of water in a twelve-ounce covered beaker. Filter and wash. Extract any possible zinc sulphide, etc., from the residue, by dissolving in nitric acid, boiling off hydrogen sulphide, and adding this to the first filtrate obtained after evaporating to dryness with nitric acid. The sodium sulphide solution contains the tin and phosphorus. Add to it hydrochloric acid until just acid. Warm slightly and pass hydrogen sulphide. Filter off stannous sulphide and wash thoroughly with hot water. Burn off in a porcelain crucible and weigh stannic oxide. Calculate to metallic tin. The filtrate from the stannous sulphide is boiled to expel hydrogen sulphide and then oxidized by adding two cc. of nitric acid and boiling for fifteen minutes more. Filter off any sulphur which separates, and in this filtrate, which should amount to only about 100 cc., precipitate the phosphorus by adding pure sodium hydroxide solution till alkaline, then nitric acid till distinctly acid, heating to 85° C., and adding fifty cc. of filtered molybdate solution. Stir or shake well for five minutes, filter on a weighed filter paper, and after washing with one per cent. nitric acid wash, dry at 100° C. and weigh. Yellow precipitate multiplied by 0.0163 equals phosphorus. The nitric acid solution obtained after evaporating the first solution to dryness, etc., is now neutralized with sodium hydroxide solution, and then made just acid with hydrochloric acid. Ten grams of sodium acetate are now added, and 300 cc. of water (hot). Boil up for five minutes, then filter and wash. If the precipitate is of considerable size, it is probable that aluminum was a constituent of the solder. Redissolve it in a little hydrochloric acid, neutralize, acidify, and make a basic acetate separation as before. Precipitate the zinc in the acetate solutions by hydrogen sulphide.

Filter, wash, ignite in a porcelain crucible, and weigh as zinc oxide. Calculate to metallic zinc. Dissolve the precipitate of aluminum acetate in hydrochloric acid, dilute to 250 cc., and precipitate with ammonia. After filtering, washing, igniting, and weighing as alumina, calculate to metallic aluminum. Solders containing lead are sometimes met with. In such cases, evaporate the nitric acid filtrate from the metastannic acid to small bulk, add twenty-five cc. of twenty-five per cent. sulphuric acid, and evaporate until white fumes escape. Cool, add 100 cc. of water, stir, and let stand for an hour in a warm place. Filter and wash with water containing five per cent. of sulphuric acid. Burn off in a porcelain crucible at a low temperature. Reoxidize any reduced lead oxide and restore its sulphur trioxide by adding a few drops of nitric acid and sulphuric acid and evaporating. Finally weigh lead sulphate. Calculate to metallic lead. Zinc is determined in the lead sulphate filtrate.

ANALYSIS OF ALUMINA.

Alumina is made from bauxite or cryolite. It is usually purchased in the hydrated form.

HYDRATED ALUMINA.

Hydrated alumina is analyzed for water, silica and sodium carbonate.

Water.—Ignite one gram in a closely covered crucible, at first gently and then intensely for fifteen minutes over the strongest blast. The loss on ignition includes water and the carbon dioxide of the sodium carbonate. Calculate the carbon dioxide from the sodium oxide found and deduct it from the loss on ignition.

Silica.—Hydrated alumina is soluble in sulphuric acid of 42° B. The silica, however, is left undissolved. 42° B. sulphuric acid is made by mixing 900 cc. of concentrated sulphuric acid with 1290 cc. of water. Five grams of hydrated alumina are treated with twenty-five cc. of 42° B. sulphuric acid and heated until the alumina appears to be all dissolved. Dilute to 100 cc. and boil. Filter, wash, ignite and fuse the residue with one gram of potassium bisulphate and cool. Dissolve in water, filter, wash, ignite, and weigh in crucible, treat with sulphuric acid and hydrofluoric acid, evaporate, ignite and weigh again. Loss equals silica.

Soda.—The method for the determination of soda is the same in calcined and hydrated alumina. The method is that of J. L. Smith, and is described under "Sodium in Aluminum." Calculate sodium chloride to sodium carbonate, if the sample is hydrated, and to sodium oxide if the sample is calcined alumina.

CALCINED ALUMINA.

Water and soda are determined as in hydrated alumina.

Silica.—Fuse one gram of the finely ground alumina with ten grams of potassium bisulphate. If this does not make a clear fusion add two grams of bisulphate and heat up again. Dissolve the fusion when cool in water and filter. Burn off the insoluble residue. Fuse it with one gram of sodium carbonate and cool in fifteen cc. of water in a four and a half inch evaporating dish. Add twenty-five cc. of twenty-five per cent. sulphuric acid. When all soluble matter has dissolved, remove the crucible and evaporate down until sulphuric acid fumes escape. Cool, dilute with water, boil, filter, ignite, and weigh silica plus crucible, treat with sulphuric and hydrofluoric acids, and weigh again. Loss equals silica.

ANALYSIS OF BAUXITE.

Method adopted, May, 1895.

No unusual apparatus or reagents are required.

One and five-tenths grams of very finely ground bauxite (previously dried at 100° C. and bottled), is taken for analysis. Weigh into a five inch porcelain evaporating dish and dissolve in fifty cc. of acid mixture. This mixture is the same as that used for aluminum analysis. Boil the solution down until fumes escape and keep the residue fuming strongly for about fifteen minutes. Cool, add 100 cc. of water, stir and then boil for ten minutes. Filter, wash well with water, receiving the filtrate in a beaker of about 300 cc. capacity. The filtrate and washings should amount to about 175 cc. Burn off the insoluble residue (which consists chiefly of silica, with a little titanic acid, oxide of iron, and alumina) and weigh it in the crucible, add three drops of twenty-five per cent. sulphuric acid and about five cc. of hydrofluoric acid and evaporate slowly to dryness. Ignite very strongly and weigh. The loss in weight equals silica. Add to the residue in the crucible one gram of potassium bisulphate and fuse quickly and thoroughly over a Bunsen burner, cool and place the crucible in the beaker containing the main sulphuric acid solution. The small residue from this fusion will be silica, and is to be added to the silica already found. Having obtained the sulphate solution containing all the alumina, ferric oxide and titanic oxide, make it up to 550 cc. and mix. Then fifty cc. will equal three-tenths gram bauxite. Take fifty cc. and dilute to 300 cc. Add two cc. of concentrated hydrochloric acid and ammonia in slight excess, boil for five minutes, let the precipitate settle, filter and wash very thoroughly with hot water. Test the filtrate for further alumina by boiling. Burn off the filter paper and ignite the precipitate very strongly after crushing all the lumps of alumina. Weigh alumina, ferric oxide and titanic oxide.

Titanic Acid.—Take 100 cc. of the original sulphate solution (six-tenths gram), add ammonia until a slight permanent precipitate is formed, then add sulphuric acid from a pipette or burette until this precipitate just redissolves. Finally add one cc. more of twenty-five per cent. sulphuric acid and dilute to 400 cc. If the bauxite is high in iron (which will be indicated by the distinct yellow color of this solution) sulphur dioxide gas must be run into it until it is decolorized and smells strongly of sulphur dioxide, but if the solution is nearly colorless, indicating a low percentage of iron, only sulphur dioxide water need be used for the reduction. Boil well for one hour, adding water saturated with sulphur dioxide occasionally. Filter off the titanic oxide through double filters and wash well with hot water. If the precipitate is yellow, indicating the presence of iron, it can be fused with one gram of potassium bisulphate, the fusion dissolved in water, and the iron determined in this solution by reducing with zinc and titrating with permanganate. This is not often necessary.

Oxide of Iron.—Take fifty cc. of the sulphate solution, add ten cc. of dilute sulphuric acid and one gram of granulated zinc, and set the beaker in a warm place. When reduced, filter and titrate the iron with standard potassium permanganate. More zinc is used for bauxites high in iron.

METHOD FOR IRON DETERMINATION, USING A LARGER QUANTITY OF BAUXITE. (APPLICABLE TO PUREST ORES).

Place a half gram of the finely powdered ore in a large platinum crucible and add three cc. of twenty-five per cent. sulphuric acid and five cc. of hydrochloric acid, and evaporate very slowly to fumes; drive off the excess of sulphuric acid by heat, boil out the residue with water and add ten cc. of dilute sulphuric acid. Remove the crucible and reduce with zinc, as above, and titrate.

Water and Organic Matter.—Ignite three-tenths gram, cautiously at first and finally very strongly in a covered crucible. The loss of weight equals water and organic matter.

ESTIMATION OF THORIA. CHEMICAL ANALYSIS OF MONAZITE SAND.

BY CHARLES GLASER.

Received July 9, 1896.

SINCE the introduction of the Auer-Welsbach light, the commercial importance of monazite sand has grown greatly, and chemists are now asked to determine the percentage of true monazite, and especially that of thoria, in samples of the sand. This has heretofore been accomplished indirectly; the quantities of iron, titanium and silica were determined and the remainder of the material calculated as monazite. A sample treated in this manner gave the following results:

	Per cent.
Iron oxide	3.50
Titanic acid	4.67
Silica	6.40
Monazite, by difference	85.43
	100.00

The sample contained 18.38 per cent. phosphoric acid, which calculated as cerium phosphate (factor 3.32) equals 61.10 per cent.

From analyses printed in Dana's Mineralogy, it was inferred that after elimination of rutile and silica, the remainder would be found to consist chiefly of phosphates of the cerium group, but this is not true.

For the determination of the actual composition of the monazite sand in question, it was decided to attempt an estimation of each of its components, by means of methods to be found in the available literature. As chief sources of information, Graham-Otto's Chemistry and Crookes' Select Methods in Chemical Analysis were used; due regard was also given to the work which has appeared in the chemical journals of recent years. I was not able, however, to make an exhaustive examination of the literature.

It became evident that no reliable method could be worked out until examination had been made of all the work which had been done in the field, and it seemed necessary to investigate the whole question. In the following statements of preliminary experiments a large portion of analytical data has been omitted, because otherwise this paper would have been bulky. Only the outlines of a general plan of procedure will therefore be given.

So far as possible, it was my intention to examine all the methods proposed for estimation of thoria, but in one notable instance this could not be done. In Volume XVI of the *American Chemical Journal*, L. M. Dennis and F. L. Kortright describe a method for estimation of thoria by means of potassium hydronitride, KN_3. An attempt to work by the method proved a failure in my hands, partly because of a mishap while preparing the reagent, only enough of which was saved for a single qualitative reaction; but chiefly because Mr. Dennis declined, when requested, to give me further information. He replied that he was not then at liberty to detail his experience, "as the potassium hydronitride process is more than an analytical one. It is a commercial process for the preparation of pure thoria, which is, I think, unequalled by any of the methods employed by the Welsbach chemists, Shapleigh included. Some of them have tried to use the method and have failed. I think I know why they failed. But I do not think it quite fair for them to ask me to help them out of their difficulties."

Although the publication was made in a scientific journal, it seems to have been but a partial statement. For which reason criticism is invited and the value of the work is thrown somewhat in doubt. No further attempt was made to follow it out.

By means of fusion with alkali carbonates, an attempt was made to separate monazite sand into two parts. According to Wöhler all titanic acid ought to become soluble provided the fusion is made at a sufficiently high temperature. Therefore a blowpipe was used. In later work I employed the highest temperatures afforded by a muffle, and for as many as two hours. But at no time was more than a fraction of the titanic acid rendered soluble in water. Moreover, Wöhler's directions to pour the fusion upon an iron plate, and afterwards to powder it, are not practicable because of loss likely to ensue. It was found best to let the fusion soak in water over night, sometimes even for several days, or until perfect disintegration resulted. But such a procedure may have decreased the solubility of titanic acid in water. Phosphoric acid and alumina (and also silica to a large extent) were completely dissolved out of the fused mass. The portion insoluble in water was rendered soluble by the well known treatment with strong sulphuric acid, and also by fusion with acid potassium sulphate. The solution thus obtained, after being freed from silica, was boiled to separate titanic acid, from four to seven hours during the first experiment. Later, after addition of sodium sulphite, this was accompanied by saturating with hydrogen sulphide, first in the hot and then in the cooled solution. This method is preferable to the first.

After separation of titanic acid and the metals of the fifth group, various methods were tried for separation of thoria from the other earths. It was found that the solution must not be strongly acid when treated with ammonium oxalate for precipitation of thoria and the metals of the cerium group, or traces of thoria will remain in solution. It is best to nearly neutralize with ammonia, and to precipitate in boiling solution.

During the earlier experiments some difficulty was found in keeping in solution all of the zirconia, which is accomplished only by a large excess of the reagent, while yttria and glucina readily form soluble double salts. Under these conditions oxalates of the cerium metals precipitate immediately, while thorium oxalate separates upon cooling. Attempts to separate thorium oxalate from oxalates of the metals of the cerium group by filtration of the hot solution, gave unsatisfactory results. The oxalates will pass through the filter for a long time. Bumping of the liquid made it impracticable to keep it boiling until the entire precipitate became crystalline. But if large quantities of thoria are to be separated from small ones of the other oxalates the method works well.

After the insoluble oxalates were separated by filtration and were washed with water, they were converted into oxides by heating and were redissolved as sulphates. In this strongly concentrated solution, made nearly neutral by ammonia, an attempt was made to separate thoria from the other metals by boiling with sodium hyposulphite. In no instance was a complete separation effected, but such portions as were obtained proved to be quite pure. The single exception was that in which the whole of the cerium was precipitated, for reasons not ascertained. Attempts were made to free thoria from most of the cerium by fractional precipitation with weak ammonia, but no considerable advantage was gained thereby, since repeatedly the second fraction showed traces of thorium.

To determine the solubility or insolubility of the different substances left in the insoluble residue from fusions, such residue was treated with dilute hydrochloric acid both cold and hot. The solution was found to contain all the iron and titanium, the larger part of the silica, and about one-half of the earths present; these consisted of relatively large portions of zirconia and glucina. Thoria seems not to enter into solution, but is left with the remainder of the earths.

An attempt was made to separate thorium oxalate from the mixed precipitated oxalates, by boiling with ammonium oxalate. Such boiling, filtering and crystallizing yielded oxalates, which after ignition, corresponded to 2.29 per cent. of oxides. The earths were, however, of a deep orange color, and contained both cerium and zirconia. The latter was present because an insufficient quantity of ammonium oxalate had been used in the first precipitation. In the oxalates of the cerium metals found insoluble in the above treatment, the presence of thoria could be distinctly proven by means of sodium hyposulphite, for which reason the work proved unsatisfactory.

To facilitate a comparison of the more important reactions of the elements herein studied, the table on the next page has been prepared partly from their known behavior, and partly from the results obtained during this investigation.

With the view of obtaining further knowledge of the behavior of thoria, fragments of Welsbach mantles were subjected to analysis. They weighed 0.6591 gram, which, after ignition, fell to 0.6552 gram. Prolonged treatment with boiling sulphuric acid left a residue of 0.0883 gram, which became soluble in water after fusion with acid potassium sulphate. The solutions thus obtained were examined by the same method, but separately, as follows: After neutralizing with ammonia the greater part of the free acid, the solutions were heated to boiling and hot solution of ammonium oxalate was added.

In solution I a precipitate appeared, but dissolved rapidly upon addition of more of the reagent.

In solution II a slight turbidity appeared, there was no precipitate, and it soon became perfectly clear.

Upon cooling, solution I yielded a moderate quantity of a crystalline deposit, while solution II gave a copious one. Both precipitates were collected on one filter, washed, ignited, and weighed. They yielded 0.1124 grams of thoria.

The filtrate from I gave a copious precipitate with ammonia, while that from II gave only a slight one: both of these were washed on one filter, redissolved in dilute hydrochloric acid, and again precipitated by ammonia. An excess of ammonium carbonate entirely dissolved the precipitate. Potassium hydroxide gave a precipitate not soluble in excess of the precipitant, indicating zirconia, the weight of which was 0.5580 gram. An attempt to purify it from occluded alkali, by again precipitating with ammonia, failed through an accident, in which part of the material was lost. Calculating by difference, the weight of zirconia ought to have been 0.5428 gram. Both precipitates were pure white.

Therefore, this analysis afforded the following composition of the mantles: thoria 17.15 per cent., zirconia 82.85 per cent.

TABLE OF REACTIONS OF THE RARER EARTHS.

	KOH or NaOH	K_2CO_3 or Na_2CO_3.	K_2SO_4 or Na_2SO_4.	$Na_2S_2O_3$.	NH_4OH.	$(NH_4)_2CO_3$.	NH_4Cl.	$(NH_4)_2C_2O_4$.	$NH_4C_2H_3O_2$.
Al_2O_3	Ppt., sol. in excess.	Ppt.	Alums.	Ppt. in boiling almost neutral solution.	Ppt.	Ppt.	Ppt. from solution in NaOH.	No ppt.	Nearly neutral solution boiled gives ppt. of basic salt.
BeO_2	Ppt. sol. in excess. Reppt. when boiled or diluted.	Ppt. with difficulty sol. in large excess and in CO_2.	No ppt., no double salt formed. Sol. with difficulty.	No. ppt.	Ppt. insol. in excess.	Ppt. easily sol. in excess. Ppt. on boiling. Uncertain separation from Al_2O_3.	Hydroxide diss. on prolonged boiling NH_3 escapes.	No ppt., double salt easily sol.	?
ZrO_2	Ppt. insol. in excess.	Ppt. slightly soluble in excess. Ppt. by NH_4OH.	Double salt sol. in hot solution. Ppt. of basic salt on cooling, insol. in HCl.	Ppt. hydroxide mixed with S.	Ppt. insol. in excess.	Ppt. sol. in large excess. Reppt'd. on boiling.	No ppt.	Ppt. sol. in excess.	?
Gadolinite earths.	Ppt. insol. in excess.	Ppt. sol. in excess. After some hours insol. double salt separates (Yt).	Conc. solution ppt. sol. in H_2O or K_2SO_4 (not Yt.) Sept. from thoria and cerites.	?	Ppt. insol. in excess.	Ppt. easily sol. in excess. Ppt. insol. double salt after some hours (Yt).	?	Ppt. red granular powder (Er.) from boiling acid solution.	?
ThO_2	Ppt. insol. in excess.	Ppt. sol. in excess. Turbid on heating, clears on cooling.	Double salt insol. in saturated solution K_2SO_4. Sodium salt much more sol.	Only partial ppt., even on long boiling conc. solution.	Ppt. insol. in excess. ThO_2 ppts. before cerites. Crookes.	Like NH_4OH.	No ppt.	Ppt. nearly insol. in acids. Sol. in excess, hot; ppt. on cooling. HCl ppts.	No ppt. prevents completely ppt'n. by $(NH_4)_2C_2O_4$ Partial ppt. by HCl, complete by excess NH_4OH.
CeO	Ppt. insol. in excess.	Ppt. slightly sol. in excess.	Double salt insol. in K_2SO_4 solution.	No. ppt. (?)	Ppt. insol. in excess.	Like NH_4OH.	No ppt.	Ppt. even in rather acid solution. Slightly sol. in large excess of acid.	Oxalate insol.
Ce_2O_3	Excess gives flesh colored ppt.	Ppt. nearly insol. in excess.		No. ppt.	Like KOH.	Ppt. sol. in large excess. Reppt'd. on boiling.	No ppt.	Like CeO.	Oxalate insol.
La_2O_3	Ppt. insol. in excess.	Ppt. nearly insol. in excess.	Double salt sol. with difficulty.	No. ppt.	Ppt.	White ppt. quite insol. in excess.	No ppt.	Ppt. in neutral or ammoniacal (?) solution.	Oxalate insol.
Di_2O_3	Ppt. insol. in excess.	Ppt. nearly insol. in excess.	Double salt sol. with difficulty.	No. ppt.	Ppt.	Rose colored ppt. quite insol.	No ppt.	Ppt. nearly insol. in oxalic or mineral acids.	Oxalate insol.

The separation of the two earths was effected without difficulty and the thoria was used in the following experiments:

0.0487 gram was weighed, dissolved, and mixed with the solution of cerium metals from a previous experiment. The solution was nearly neutralized with ammonia, heated to boiling, a hot solution of ammonium oxalate added, and the mixture allowed to cool. The precipitate was caught on a filter and washed with cold water, extracted in boiling ammonium oxalate solution, caught on a filter, and washed hot: the filtrate was allowed to cool (precipitate 1). The residue was macerated in a hot solution of ammonium acetate, filtered (residue A), and filtrate examined for thoria, as follows: hydrochloric acid was added to separate thoria as oxalate, which fell in part only and the remainder was obtained by sodium hydroxide (precipitate 2). Both these precipitates afforded but a part of the thoria originally weighed, the greater part being held yet with the cerium metals. The method had failed.

The residue (A) upon the filter was reduced to oxide and dissolved as sulphate. After neutralizing with ammonia, the liquid was heated to boiling, and there was added an excess of ammonium oxalate with some ammonium acetate: after filtering, the filtrate was treated with sodium hydroxide (precipitate 3).

The precipitates, thus obtained in three fractions, were ignited and found to weigh 0.0774 gram, showing that the thoria was very impure. The grayish mass was fused with acid potassium sulphate, and unfortunately, a small fraction of the fused mass was lost. However, from the saved portion a pure thoria, weighing 0.0402 gram. was obtained.

In the next experiment, 0.0343 gram of thoria and 0.1004 gram of impure cerium oxide were dissolved as sulphates, and treated with ammonium oxalate and acetate, as for precipitate 3, next above. By precipitating the filtrate with ammonia there was obtained 0.0360 of impure thoria, which, after purification, weighed 0.0344 gram. Cerium oxide recovered weighed 0.0935 gram.

I desire to call attention to what has been observed frequently during these experiments. If thorium oxalate, held in solution by ammonium acetate, be precipitated by ammonia, the earth so obtained, when washed with the greatest care and redissolved in a mineral acid, cannot from an almost neutral solution be again completely precipitated by ammonium oxalate; even if the earth had been ignited after re-solution. It will also be found that a considerable increase has occurred in its solubility in liquids containing much potassium or ammonium sulphate. When enough thoria has been collected, it is my intention to further examine this peculiar behavior.

SYSTEMATIC METHOD OF ANALYSIS.

From the analytical data given, the following method has been deduced:

It is essential that the mineral be divided to the greatest possible degree. Prolonged powdering in an agate mortar is indispensable. Solution is effected either by prolonged heating with strong sulphuric acid, or by fusion with acid potassium sulphate. In the latter case, the cooled mass is warmed with so much sulphuric acid that the product, after cooling, may be poured from the crucible. The first method takes more time than the second, but it introduces less of the objectionable potassium salts. It is advisable to fuse only those portions which are insoluble in sulphuric acid.

For estimation of silica the sulphuric acid treatment is preferable, in which case it is best to evaporate once on a sand-bath to dryness to render silica insoluble, and then to add fresh sulphuric acid. The resulting mixture should be added slowly to ice cold water, which dissolves the mass excepting silica and tantalic acid, with possibly traces of titanic acid, thoria, and zirconia. After filtering, the residue should be ignited and weighed. Silica is eliminated by repeated treatment with hydrofluoric acid. Any residue remaining should be moistened with sulphuric acid, to convert the fluorides of the earths into sulphates, which, after ignition at a high temperature, are weighed as oxides, and silica determined by the loss in weight. The residue of tantalic acid, with possibly traces of the bodies mentioned above, is treated with sulphuric acid and hydrofluoric acid. Tantalic acid remains insoluble, and may be filtered off and weighed. The matter soluble may be added to the main solution.

The original solution is saturated with hydrogen sulphide, first at boiling and then at the ordinary temperature. Titanic acid is precipitated, together with metals of the fifth group. That sodium sulphite assists in the precipitation of titanic acid has not been verified in my work.

When completely settled, the liquid is filtered and the filtrate boiled to expel hydrogen sulphide. Any free acid may be nearly neutralized with ammonia; to the boiling liquid is added an excess of a boiling solution of ammonium oxalate, as much as 100 cc. of the cold saturated solution for two grams of monazite sand. The excess necessarily must be large. The mixture is then permitted to cool, best for an entire night. The solution will contain phosphoric acid, the oxides of iron, manganese, aluminum, glucinum, yttrium, zirconium, and calcium. In the precipitate will be found thoria and the oxides of the cerium group.

If the bodies in solution are to be estimated, add ammonia to precipitate the metals as phosphates. Filter and wash thoroughly, preserve the filtrate for estimation of phosphoric acid and alumina. Ignite the precipitate and fuse it with mixed carbonates of potassium and sodium. The fused mass is exhausted with hot water, filtered, and the residue well washed with hot water. The filtrate is added to that containing phosphoric acid and alumina.

The remaining oxides and carbonates are dissolved in sulphuric acid and precipitated with ammonia. Lime is estimated in the filtrate therefrom.

When an attempt is now made to dissolve the precipitated hydroxides on the filter by dilute hydrochloric acid, it sometimes occurs that zirconia in part remains. Therefore it is best, after this operation, to incinerate the filter. Then neutralize the solution with ammonia as far as practicable. Pour this slowly, with constant stirring, into a mixture of ammonium carbonate and ammonium sulphide, prepared as follows: To a solution of ammonium carbonate more than enough to neutralize the free hydrochloric acid above indicated, and to hold in solution the earths to be dealt with, add enough of ammonium sulphide (usually a few cc.) to precipitate the metals of the fourth group. The latter will be precipitated, while zirconia, yttria, and glucinum remain in solution. Iron and manganese may be determined by the usual methods.

If the carbonate solution be boiled for one hour the earths are completely precipitated. They may be caught on a filter and dissolved in hydrochloric acid; or the carbonate solution may be treated directly with that acid, carbon dioxide expelled by boiling, the solution cooled and treated with an excess of sodium hydroxide. Zirconium and yttria are completely precipitated while glucina remains dissolved: to precipitate this, boil the solution one hour.

To separate zirconia from yttria, dissolve the hydroxides in hydrochloric acid, warm, then saturate the solution with sodium sulphate. When cold, zirconia separates in the well-known manner. From the filtrate ammonia separates yttria.

As the earths are apt to occlude alkali salts, it is best to dissolve and again precipitate them (with ammonia) before they are ignited and weighed.

Separation of the precipitated oxalates of thoria and of the cerium group is accomplished as follows: The oxalates are reduced to oxides by ignition, then converted into sulphates, the greater part of the free acid neutralized with ammonia, the solution boiled, and boiling ammonium oxalate added in excess. After a short time (as soon as oxalates of the cerium metals have formed but before the liquid has cooled), a few cc. of solution of ammonium acetate are added. When cold, the entire cerium group is precipitated as oxalates, while thoria remains in solution. After prolonged standing, best over night, the insoluble oxalates are removed by filtration; in the filtrate, precipitate thoria with ammonia in excess, filter, ignite, and weigh.

Separation of cerium from lanthanum and didymium is easily accomplished by the well known method. Pass a current of chlorine through the liquid containing the hydroxides, which have been freshly precipitated by a fixed alkali.

Separation of lanthanum from didymium was not attempted.

An analysis of the monazite sand used in my work, made as indicated in the foregoing notes, gave results as follows:

Titanic acid	4.67
Silica	6.40
Phosphorus pentoxide	18.38
Lead	trace
Alumina	1.62
Lime	1.20
Cerium oxide (CeO)	32.93
Lanthanum and didymium oxides	7.93
Thoria	1.43
Ferric oxide	7.83
Zirconia and yttria	13.98
Glucina	1.25
Tantalic acid	0.66
Not determined	1.72
	100.00

Titanic acid and silica was determined in a separate portion. The determination of tantalic acid was only approximate, since a part of it is dissolved by fusion with acid potassium sulphate, and thus escapes weighing. As several such fusions were made, it is probable that the greater part of the matter "not determined" ought to be reckoned as tantalic acid. The quantity stated was an average of three determinations (minus or plus 0.05) from the residue of repeated fusions.

Through the courtesy of Mr. H. B. C. Nitze, of the Geological Survey of North Carolina, I have received a number of samples of monazite sand mined at various localities in that state. Two of these had been prepared by a new process and were found to be practically free from rutile and garnets. They were excellent material for my methods of analysis, and they gave results as follows:

ANALYSIS OF A COARSE MONAZITE SAND FROM SHELBY, NORTH CAROLINA.

Silica	3.20
Titanic acid	0.61
Cerium metals as CeO	63.80
Phosphorus pentoxide	28.16
Thoria	2.32
Zirconia, glucina, yttria	1.52
Manganese	trace
No iron, alumina, or lime	0.00
	99.61

The color of this sand was honey-yellow.

ANALYSIS OF A FINE MONAZITE SAND FROM BELLEWOOD, NORTH CAROLINA.

Silica	1.45
Titanic acid	1.40
Cerium metals as CeO	59.09
Phosphorus pentoxide	26.05
Thoria	1.19
Zirconia, glucina, yttria	2.68
Tantalic acid	6.39
Iron and manganese oxides	0.65
Alumina	0.15
	99.05

The color of this sand was honey-yellow.

LABORATORY OF LEHMANN & GLASER,
BALTIMORE.

[CONTRIBUTIONS FROM METALLURGICAL LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO.]

THE EFFECT OF AN EXCESS OF REAGENT IN THE PRECIPITATION OF BARIUM SULPHATE.

BY C. W. FOULK.

Received July 6, 1896.

"EXCESS of reagent" is a term often used by writers in quantitative chemistry, and the necessity in any given case for adding more of a precipitating reagent than is just sufficient for complete reaction is well known to analysts; but what constitutes such excess, whether it differs for different salts, whether its effect is counteracted by the presence in the solution of other bodies not taking part in the reaction, or whether the effect of such bodies may be counteracted by the addition of a greater amount of precipitant, etc., etc., are questions, the answers to which are difficult to find in chemical literature.

With a view to answer, in part at least, these questions, the following work on the precipitation of barium sulphate was undertaken.

A preliminary experiment, which perhaps is worth noting, was first tried:

A solution of 140 cc. water and five cc. concentrated hydrochloric acid was heated nearly to boiling and 0.1984 gram pure recently ignited barium sulphate was added. This was then stirred up and set aside for one hour, when it was filtered and the barium sulphate washed well with hot water. The filter and the contents were then ignited and weighed, when it was found that ten milligrams of the sulphate had been dissolved. The filtrate was now divided, and to one-half some sulphuric acid was added, and to the other some barium chloride solution. *A precipitate of barium sulphate was produced in both cases.*

Standard solutions of sulphuric acid and barium chloride were now prepared. These were standardized by precipitation from pure water solutions.

The sulphuric acid used in this work was the chemically pure acid of the laboratory, tested for the ordinary impurities.

The barium chloride was recrystallized from the chemically pure salt.

The hydrochloric acid was the chemically pure acid of the laboratory tested for sulphuric acid.

The graduated ware was calibrated and found to be good.

All the precipitates of barium sulphate were ignited by folding up the moist filter, putting into a platinum crucible, "precipitate end" up and so adjusting the flame that the paper would be charred away without letting the crucible become red hot. Finally the heat was raised and the ignition finished. No lid was used on the crucible. By following this plan no reduction to sulphide need be feared.

A number of the precipitates were moistened with sulphuric acid and ignited. No change was noticed.

In the course of the work the following solutions were made:

SULPHURIC ACID SOLUTION.

Solution A.

	cc.	Barium sulphate.
1.	20	0.1978
2.	20	0.1975
3.	20	0.1970
4.	20	0.1978
	Average	0.1970

Solution B.

	cc.	Barium sulphate.
1.	50	0.3277
2.	50	0.3271
3.	50	0.3279
	Average	0.3275

Solution C.

	cc.	Barium sulphate.
1.	5	0.1944
2.	5	0.1940
	Average	0.1942

Solution D.

	cc.	Barium sulphate.
1.	25	0.1544
2.	25	0.1534
3.	25	0.1543
4.	25	0.1538
5.	25	0.1535
6.	25	0.1546
7.	25	0.1539
	Average	0.1542

Rejecting Nos. 2 and 5.

BARIUM CHLORIDE SOLUTIONS.

Solution A.

	cc.	Barium sulphate.
1.	20	0.1181
2.	20	0.1812
3.	20	0.1811
4.	20	0.1792
5.	20	0.1802
	Average	0.1805

Rejecting No. 4.

Solution B.

	cc.	Barium sulphate.
1.	50	0.1985
2.	50	0.1980
3.	50	0.1086
4.	50	0.1985
	Average	0.1984

Solution C.

	cc.	Barium sulphate.
1.	10	0.4004
2.	10	0.4002
3.	10	0.4006
	Average	0.4004

Solution D.

	cc.	Barium sulphate.
1.	10	0.3998
2.	10	0.3994
3.	10	0.3996
	Average	0.3996

Note.—The apparent discrepancies in some of the above averages are to be explained by the fact that before beginning the work the burette used had been very carefully calibrated, and the averages were calculated to correct number of cubic centimeters from the readings as given on the burette. In the course of the work this refinement was found to be wholly unnecessary and was therefore disregarded.

The equation of solutions of sulphuric acid and of barium chloride is: Twenty cc. barium chloride solution = 21.8 cc. sulphuric acid. That is, when mixed in these proportions they will, theoretically, mutually precipitate each other and give 0.1970 gram barium sulphate.

The effect of bringing these two solutions together in this proportion was first tried. The barium chloride solution plus water to make the whole volume up to 140 cc. was heated to boiling and the sulphuric acid run in from the burette.

		Barium sulphate.	Error.
1.	20 cc. $BaCl_2$*A*+21.8 cc. H_2SO_4*A*	0.1966	−0.0004
2.	20 " " " " "	0.1973	+0.0003
3.	20 " " " " "	0.1979	+0.0009

Solutions of $BaCl_2$*B* and H_2SO_4, when brought together in their molecular proportions, weighed as follows:

		Barium sulphate.	Error.
1.	50 cc. $BaCl_2$*B*+ 30.2 cc. H_2SO_4*B*	0.1979	−0.0005
2.	50 " " " " "	0.1976	−0.0008

These had stood twenty-two hours before filtration, and the results, while not very close, show at least that in water solutions precipitation is practically complete without the presence of an excess of reagent.

A series of precipitations was now made in order to determine the effect of varying quantities of hydrochloric acid upon the precipitation when the two reagents were brought together in their molecular proportions.

The barium chloride solution, water to make the volume up to 140 cc., and the hydrochloric acid were heated to boiling and the sulphuric acid run in cold from the burette.

The same quantities of barium chloride and sulphuric acid were used as above. The time of standing before filtration is marked over each set. Three precipitations were made with each portion of the hydrochloric acid.

SERIES I.

	1. Five cc. hydrochloric acid. Twenty-five hours. Barium sulphate.	2. Ten cc. hydrochloric acid. Twenty-nine hours. Barium sulphate.	3. Fifteen cc. hydrochloric acid. Thirty-three hours. Barium sulphate.	4. Twenty cc. hydrochloric acid. Forty-four hours. Barium sulphate.
1	0.1908	0.1879	0.1827	0.1875
2	0.1902	0.1870	0.1844	0.1863
3	0.1904	0.1881	0.1838	0.1873

It was thought that after standing twenty-four hours precipitation would be complete and a longer time would have no effect. The results of series No. 4 seem to show differently, however. Accordingly another series was run in which the time of standing was regulated. Otherwise the precipitations were made as above.

These stood twenty-three hours before filtration.

SERIES II.

	1. Five cc. hydrochloric acid. Barium sulphate.	2. Ten cc. hydrochloric acid. Barium sulphate.	3. Fifteen cc. hydrochloric acid. Barium sulphate.
1	0.1902	0.1870	0.1852
2	0.1884	0.1854	0.1849
3	0.1904	0.1846	0.1827

	4. Twenty cc. hydrochloric acid. Barium sulphate.	5. Twenty-five cc. hydrochloric acid. Barium sulphate.	6. Thirty cc. hydrochloric acid. Barium sulphate.
1	0.1832	0.1822	0.1766
2	0.1885	0.1793	0.1833
3	0.1850	0.1789	0.1733

The above results show three things: (1) That less barium sulphate is precipitated in the presence of larger amounts of hydrochloric acid, but this solubility is not proportional to the amount of hydrochloric acid. (2) That the greatest variation of results takes place in the presence of the larger amounts of acid. In other words parallel precipitations don't "check." (3) A much longer time is required to reach the maximum of precipitation in the presence of the larger amounts of hydrochloric acid. See No. 4, Series I.

The effect of a small excess of sulphuric acid was now tried. Three solutions each containing fifty cc. barium chloride *B*, sixty cc. water and twenty cc. hydrochloric acid were heated to boiling and the amounts of sulphuric acid *B*, indicated below, were run in from a burette.

These stood twenty-four hours and weighed as follows:

SERIES III.

		Barium sulphate.	Error.
1.	50 cc. $BaCl_2$ *B* + 31.2 cc. H_2SO_4 *B* = 1 cc. excess	= 0.1839	—0.0145
2.	50 " " + 32.2 " " = 2 " "	= 0.1881	—0.0103
3.	50 " " + 33.2 " " = 3 " "	= 0.1971	—0.0013

The filtrates from the above gave no further precipitate on standing several days.

Another series was run, using five cc. hydrochloric acid instead of twenty cc., but conducted otherwise in the same manner except that they stood from Friday to the following Monday and undoubtedly the maximum of precipitation was reached.

SERIES IV.

		Barium sulphate.	Error.
1.	50 cc. $BaCl_2$ *B* + 31.2 cc. H_2SO_4 *B* = 1 cc. excess	= 0.1951	0.0033
2.	50 " " " + 32.2 " " " = 2 " "	= 0.1963	0.0021
3.	50 " " " + 33.2 " " " = 3 " "	= 0.1964	0.0020

It was now decided to use larger amouuts of sulphuric acid in excess, but in order to hurry matters along, cut down the time of standing before filtration.

In the following series, accordingly, the barium sulphate was filtered off after standing three hours. The whole volume of solution in each case was 150 cc.

SERIES V.

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *B*.	No. of cc. in excess of the theoretical am't for precipitation.	Barium sulphate weighed.	Error.
1	50	15	35.2	5	0.1458	0.0526
2	50	15	40.2	10	0.1590	0.0394
3	50	15	45.2	15	0.1688	0.0296
4	50	15	50.2	20	0.1762	0.0222

A steady increase following the larger amounts of sulphuric acid is seen, but it is to be noted that 30.2 cc. sulphuric acid in three hours did not bring down so large a precipitation as 31.2 cc. sulphuric acid did in twenty-four hours though in the presence of a larger portion of hydrochloric acid. See Series III.

In order to get comparative results the various conditions of the precipitation had to be more carefully regulated. The above results show this very plainly.

Accordingly, the following problem was set: How great an excess of sulphuric acid is required to precipitate completely as sulphate, the barium from fifty cc. of barium chloride *B*, in the presence of five cc. hydrochloric acid in one hour, the whole volume of solution, after adding the sulphuric acid, to be 150 cc.?

Instead of adding a certain number of cc. in excess the sulphuric acid was now measured in equivalents, 30.2 cc. the exact amount to precipitate fifty cc. barium chloride was called one equivalent and different multiples of it were taken.

The barium chloride, water, and hydrochloric acid were heated on the water-bath and the sulphuric acid run in cold from the burette.

SERIES VI.

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *B*.	Eqivalents sulphuric acid.	Barium sulphate.	Error.
1	50	5	37.8	1.25	0.1564	0.0420
2	50	5	45.3	1.50	0.1624	0.0360
3	50	5	52.8	1.75	0.1784	0.0200
4	50	5	60.4	2.00	0.1857	0.0127
5	50	5	68.9	2.25	0.1842	0.0142

The fact that No. 5 was lower than No. 4 was referred to the lowering of temperature produced by the addition of the sixty-eight cc. cold sulphuric acid.

The following plan was now adopted:

The sulphuric acid was measured out into beakers and also heated on the water-bath. It was then added to the barium chloride solution, the beakers being washed out three times with hot water, using about four or five cc. each time and the washings also added.

SERIES VII. (Continued from above.)

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *B*.	Equivalents sulphuric acid.	Barium sulphate.	Error.
6	50	5	67.9	2.25	0.1931	—0.0053
7	50	5	75.5	2.50	0.1935	—0.0049
8	50	5	83.0	2.75	0.1956	—0.0028
9	50	5	90.5	3.00	0.1963	—0.0021
10	50	5	39.4	4.00	0.1961	—0.0023
11	50	5	49.2	5.00	0.1962	—0.0022

Note.—The last two results were obtained with a stronger sulphuric acid solution, which was run in cold.

A rapid increase is seen with the first additions of sulphuric acid, the difference becoming less as the sulphuric acid increases.

Another peculiarity was also seen in each one of these series. Although the solutions had been well stirred on bringing the reagents together, had settled clear in a few minutes, and the supernatant liquid had remained clear, yet in running through the filter the filtrates soon became cloudy and a copious precipitate of barium sulphate settled out.

This could be due only to the agitation produced by running through the filter. Later an experiment was tried on this point. Fifty cc. of barium chloride solution, 0.0992 barium sulphate + five cc. hydrochloric acid and water to make the total volume up to 150 cc., was heated in a flask and two equivalents of sulphuric acid added. This was then shaken for ten minutes, allowed to settle for fifty minutes, and then the precipitate was filtered off and weighed.

It gave barium sulphate 0.1979, a minus error of 0.0013 as against an error of —0.0127 in Series VI, with two equivalents.

It seems that in the presence of hydrochloric acid unless there is a sufficient amount of sulphuric acid present to effect complete precipitation, a delicate balance is formed which is affected by a difference in time of standing, in temperature, and amount of agitation on stirring. To avoid adding so large a volume of sulphuric acid solution "*C*" was prepared.

Series VIII was now run. Both solutions were heated on the water-bath and brought together as described above. Solution in each case was stirred one and one-half minutes and allowed to settle one hour.

SERIES VIII.

	Barium chloride *B*.	Hydrochloric acid.	Sulphuric acid *C*.	Equivalents sulphuric acid.	Barium sulphate.	Error.
	cc.	cc.	cc.			
1	50	5	20.4	4	0.1971	—0.0013
2	50	5	25.5	5	0.1978	—0.0006
3	50	5	30.6	6	0.1981	—0.0003
4	50	5	35.7	7	0.1980	—0.0004
5	50	5	40.8	8	0.1984	0.0000
6	50	5	45.9	9	0.1985	+0.0001
7	50	5	51.0	10	0.1984	0.0000
8	50	5	56.1	11	0,1985	+0.0001

At last the proper excess to effect complete precipitation under the conditions described above had been found. Seven or eight times the theoretical amount seems necessary. It is to be noted that the change is extremely slow when near the critical point.

A short series was precipitated and weighed, using other solutions, the equation of which was as follows:

Fifty cc. $BaCl_2$, $x = 1$ cc ± H_2SO_4 $D = 0.1992$ $BaSO_4$.

SERIES IX.

	Barium chloride *x*.	Hydrochloric acid.	Sulphuric acid *D*.	Equivalents sulphuric acid.	Barium sulphate.	Error.
	cc.	cc.	cc.			
1	50	5	3	3	0.1957	—0.0035
2	50	5	4	4	0.1992	0.0000
3	50	5	5	5	0.1983	—0.0009
3	50	5	5	5	0.1992	0.0000

In this series the sulphuric acid was run in cold.

The maximum amount of precipitate seems to be reached here with less sulphuric acid than when a more dilute solution was used. The same is true of the precipitations made in the presence of ten cc. hydrochloric acid.

Series X was now run, the precipitations being made in exactly the same manner as those of Series VIII, except that ten cc. of hydrochloric acid was put into the solutions instead of five cc.

SERIES X.

	Barium chloride *B*.	Hydrochloric acid.	Sulphuric acid *C*.	Equivalents sulphuric acid.	Barium sulphate.	Error.
	cc.	cc.				
1	50	10	30.6	6	0.1964	—0.0020
2	50	10	35.7	7	0.1974	—0.0010
3	50	10	40.8	8	0.1981	—0.0003
4	50	10	45.9	9	0.1982	—0.0002
3	50	10	40.8	8	0.1970	—0.0014
4	50	10	45.9	9	0.1982	—0.0002

In the presence of ten cc. hydrochloric acid then, a somewhat greater excess of sulphuric acid is required than with five cc. hydrochloric acid.

A short series with the stronger solution gave

SERIES XI.

	Barium chloride *B*.	Hydrochloric acid.	Sulphuric acid *D*.	Equivalents sulphuric acid.	Barium sulphate.	Error.
	cc.	cc.				
1	50	10	5	5	0.1975	—0.0017
2	50	10	6	6	0.1982	—0.0010
3	50	10	7	7	0.1992	0.0000
3	50	10	7	7	0.1991	—0.0001

Series XII. was conducted exactly as Nos. VIII. and X., excepting that fifteen cc. hydrochloric acid was used.

SERIES XII.

	Barium chloride *B*.	Hydrochloric acid.	Sulphuric acid *C*.	Equivalents sulphuric acid.	Barium sulphate.	Error.
	cc.	cc.				
1	50	15	30.6	6	0.1957	—0.0027
2	50	15	35.7	7	0.1955	—0.0029
3	50	15	40.8	8	0.1965	—0.0019
4	50	15	45.9	9	0.1973	—0.0011
5	50	15	51.0	10	0.1972	—0.0012
6	50	15	56.1	11	0.1984	0.0000
7	50	15	61.2	12	0.1983	—0.0001

The point to be noted in this series is that more sulphuric acid is required in the presence of the larger amount of hydrochloric acid.

The other side of the question was now taken up, namely, the precipitation of sulphuric acid with an excess of barium chloride in the presence of hydrochloric acid.

A new difficulty at once presented itself. The old trouble in filtering barium sulphate was experienced. When a small amount of hydrochloric acid was present it was found utterly impossible to do it under the conditions which had previously been followed.

Various experiments were made to avoid this trouble and at last the following scheme was adopted:

The volume was kept at 150 cc. as in the other work. The sulphuric acid, water, and hydrochloric acid were heated on the water-bath and the barium chloride solution, also hot, was added drop by drop with constant stirring. The beakers were then set back on the bath and the solutions stirred at intervals for thirty minutes. They were then set off and stirred at intervals again until cold.

Just before pouring upon the filter the precipitate was stirred up and the filter filled several times. At first a small portion ran through, but this was poured back, and, generally, the rest could be filtered without trouble.

A series was run according to this description, except that the volume was 250 cc.

The exact time of standing before filtering was not noted in this case. It was probably about four or five hours.

SERIES XIII.

	Sulphuric acid *B*.	Hydrochloric acid.	Barium chloride *C*.	Eqivalents barium chloride.	Barium sulphate.	Error.
	cc.	cc.	cc.			
1	30.2	10	14.9	3	0.1967	—0.0017
2	30.2	10	19.8	4	0.1959	—0.0025
3	30.2	10	14.9	5	0.1965	—0.0019

There was nothing satisfactory to be derived from this series, so Series XIV was run. The volume here was kept down to 150 cc.

SERIES XIV.

	Sulphuric acid *B*.	Hydrochloric acid.	Barium chloride *C*.	Equivalents barium chloride.	Barium sulphate.	Error.
	cc.	cc.	cc.			
1	30.2	10	14.9	3	0.1975	—0.0009
2	30.2	10	19.8	4	0.1994	+0.0010
3	30.2	10	24.9	5	0.1983	—0.0001
4	30.2	10	29.8	6	0.2005	+0.0021

Two of these precipitates weigh heavier than theory demands. This could come only from contamination with barium chloride. To test this No's 3 and 4 were transferred to beakers, boiled up with about seventy-five cc. of water and again filtered, ignited, and weighed.

They then gave

3. 0.1980 barium sulphate = —0.0004 error.
4. 0.1987 " " = +0.0003 "

Another series was run in exactly the same manner, except that more care was taken in washing. Each precipitate was washed with boiling water until the filtrate no longer reacted with silver nitrate.

SERIES XV.

	Sulphuric acid *B*. cc.	Hydrochloric acid. cc.	Barium chloride *C*.	Equivalents barium chloride.	Barium sulphate.	Error.
1	30.2	10	9.9	2	0.1965	—0.0019
2	30.2	10	14.9	3	0.1982	—0.0001
3	30.2	10	19.8	4	0.1975	—0.0008
4	30.2	10	24.9	5	0.1988	+0.0004
5	30.2	10	29.8	6	0.1994	+0.0010

No's 4 and 5, on being boiled up with water and reweighed, gave

3. 0.1981 = —0.0003 error.
4. 0.1975 = —0.0009 "

At its best, however, this method of working was unsatisfactory. The precipitate seemed always on the point of running through the filter and indeed traces generally did go through.

The following scheme was accordingly tried in Series XVI.

The volume was kept as before at 150 cc., but thirty cc. of hydrochloric acid instead of ten was put into each solution. The precipitates were not stirred up after being thrown down. In presence of this large excess of acid the precipitates soon became coarse and crystalline and settled rapidly. *No trouble whatever was experienced in filtering them.*

SERIES XVI. (These had stood about four hours.)

	Sulphuric acid *E*.	Hydrochloric acid.	Barium chloride *C*.	Equivalents barium chloride.	Barium sulphate.	Error.
	cc.	cc.				
1	20	30	4.6	1.5	0.0947	—0.0289
2	20	30	6.2	2.0	0.0997	—0.0239
3	20	30	9.3	3.0	0.1114	—0.0122
4	20	30	12.4	4.0	0.1169	—0.0067
5	20	30	15.5	5.0	0.1207	—0.0029
6	20	30	18.6	6.0	0.1192	—0.0044

These filtrates, on standing over night, all showed further precipitates of barium sulphate. The series was accordingly continued, this time the solutions standing about seven hours before being filtered.

The precipitates were crystalline and filtered easily and rapidly and the filtrates, on further standing, showed no traces of barium sulphate.

In spite, however, of the greatest care in washing, it was impossible to get rid of the occluded barium chloride before ignition.

SERIES VII.

	Sulphuric acid *E*.	Hydrochloric acid.	Barium chloride *C*.	Equivl's Barium chloride.	Barium sulphate.	Error.
1	20	30	18.6	6	0.1258	+0.0022
2	20	30	21.7	7	0.1252	+0.0016
3	20	30	24.8	8	0.1268	+0.0032
4	20	30	27.9	9	0.1260	+0.0024

Nos. 2, 3 and 4 were boiled up with water, rewashed, ignited and weighed.

	Barium sulphate.	Error.	
2	0.1236	0.0000	Filtrate reacted strongly with silver nitrate.
3	0.1238	+0.0002	" " " " " "
4	0.1253	+0.0017	" " slightly " " "

No. 4 boiled up the second time 0.1237 $BaSO_4 = +$ 0.0001 error. The filtrate in this case reacted strongly with silver nitrate.

To test this boiling up process No. 4 was treated the third time. This time the precipitate weighed 0.1235 and the filtrate did *not* react with silver nitrate.

A last experiment was made to determine the effect of barium chloride upon the direct solubility of barium sulphate in hydrochloric acid.

0.1248 gram barium sulphate was put in 120 cc. water and thirty cc. hydrochloric acid and beaker marked "*A*."

0.1228 gram barium sulphate was weighed into another beaker with 105 cc. water, thirty cc. hydrochloric acid and fifteen cc. barium chloride *C*. This beaker was marked "*B*."

Both were heated on the water-bath with frequent stirring and then stood over night.

On being filtered and weighed,

"*A*" gave —0.1106 barium sulphate = 0.0142 loss.
"*B*" " —0.1228 " " = 0.000 "

To further test precipitate "*B*" it was boiled up with water as those of Series XVII, and re-weighed. It lost by this operation 0.0002, which is practically nothing.

From the results obtained in this investigation the following conclusions seem justified:

(1) In the precipitation of a barium salt with sulphuric acid in the presence of hydrochloric acid, a very large excess of sulphuric acid is required.

(2) This excess should be greater the greater the amount of hydrochloric acid present in the solution.

(3) It should be greater the shorter the time of standing before filtration. In fact a very great excess seems to effect immediate precipitation.[1]

(4) The greater the excess of sulphuric acid the less stirring seems necessary to bring down the precipitate in a given time.

(5) While barium sulphate obtained by precipitating a barium salt with sulphuric acid in the presence of hydrochloric acid is coarse, crystalline and easily filtered,[1] that obtained by precipitating sulphuric acid with a barium salt in the presence of hydrochloric acid is fine and much disposed to run through the filter unless special precautions are taken.

(6) In general a large excess of barium chloride is required to completely precipitate the sulphuric acid in the presence of hydrochloric acid.

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[1] *J. Anal. Appl. Chem.*, 5, 26.

(7) As the hydrochloric acid increases the amount of barium chloride should also be increased.

(8) The greater the amount of hydrochloric acid present the coarser and more crystalline in character is the precipitated barium sulphate. In precipitating in the presence of large amounts of hydrochloric acid the solution should be quite concentrated.

(9) The barium sulphate so obtained, will, however, be contaminated with adhering barium chloride, and no amount of washing before ignition can entirely free it from this occluded chloride. If, after ignition, the precipitate be boiled up with water, again washed, ignited and weighed, and this process be continued until a constant weight is obtained, the sulphate may be entirely freed from the barium salt.

Some subsequent work in this line has shown that heavy precipitates sometimes require three or four treatments before a constant weight is obtained.

(10) Both in the precipitation of barium with sulphuric acid and of sulphuric acid with barium, very concordant results may be obtained if the conditions under which the precipitations are made are similar, but these results may be quite far from correct. A note of this commonplace occurrence in analytical work is made here, because by following the usual method of testing the filtrate for an excess of the precipitating reagent, a strong reaction might be obtained and yet not more than ninety per cent. of the original precipitate be down.

In conclusion I wish to express my thanks to Professor N. W. Lord for helpful suggestions during the course of this work.

DISCUSSION.[1]—T. S. Gladding: I have already shown (see this Journal, **16**, 398; **17**, 181, 397, 772; **18**, 446) that correct results may be obtained if the barium chloride solution be added drop by drop instead of all at once. This is confirmed by Lane (**18**, 682) and is now virtually admitted by Lunge, who precipitates (**18**, 686) by "quick additions (*i. e.*, pouring in the hot barium chloride solution in about ten portions, occupying about half a minute in all, and stirring the mixture all the time, as every chemist would do.)"

[1] Buffalo Meeting, Aug., 1896.

THE ACTUAL ACCURACY OF CHEMICAL ANALYSIS.[1]

BY FREDERIC P. DEWEY.

Received July 14, 1896.

THE subject of this paper does not embrace the consideration of ways and means for the increase of analytical accuracy, or the question, what can be or should be attained in that direction. I desire simply to call attention to the degree of accuracy exhibited in actual every day practice. In estimating this, little weight will be given to the evidence afforded by the agreement of duplicate or multiple determinations by the same chemist; for I am convinced that such agreement is a delusion and a snare. Nor will special importance be attached to the agreement of two or even three analysts in special cases, or to the agreement between two methods practiced by the same analyst. I propose to compare the results obtained by several chemists, working upon the same sample and by various methods, in order to exhibit, as I have said, the actual condition of practice.

The available material for illustrating this phase of the question is unfortunately scanty; but something has been done; and I hope, by calling attention to some of the work in this line, to stimulate further work in the same direction by inducing others to prepare suitable samples and submit them to various chemists who are competent and willing to make the necessary determinations and fully describe the methods they employ.

I draw most of my illustrations from the "Transactions of the American Institute of Mining Engineers," the "Proceedings of the Association of Official Agricultural Chemists," and from personal experience.

MANGANESE IN STEEL.

In May, 1881, Mr. William Kent presented a paper to the American Institute of Mining Engineers entitled "Manganese Determinations in Steel,"[2] in which he gave twenty-four determinations of manganese, made by ten different chemists, employing two main methods, on samples from a plate of steel.

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[1] Read before the Washington Section of the American Chemical Society, May 14th, 1896, and published jointly with the American Institute of Mining Engineers.

[2] Trans. A. I. M. E., 10, 101.

These results presented the remarkable range of from 1.14 to 0.303 per cent., and one chemist reported results ranging from 1.14 to 0.434 per cent.

A portion of this variation was undoubtedly due to variations in the sample, since the same sample was not used throughout by the different chemists.

Throwing out the anomalous result of 1.14 per cent. we have twenty-three determinations running from 0.619 per cent. to 0.303 per cent., with an average of 0.415 per cent. Thus showing that at that time the determination of manganese in steel, when only about four-tenths per cent. was probably present, might exhibit an extreme variation between the highest and the lowest results of about three-tenths per cent., or seventy-five per cent. of the amount of manganese present.

These results were certainly very discouraging ; but if they did nothing else they served to call attention to the very unsatisfactory character of the determination of manganese in steel at that time.

I do not recall any recent symposium on the determination of manganese in this class of material, but in 1886 Capt. A. E. Hunt,[1] in giving a measure of the accuracy of the colorimetric method, speaks of a variation of 0.02 per cent. in steels containing 0.15 to one and five-tenths per cent. of manganese as "sufficiently accurate for all practical work," thus clearly intimating that the current results of analysis by other methods were at least as good. This degree of accuracy, if attained by different chemists upon the same sample, must be considered a satisfactory advance over the results reported by Mr. Kent.

Early in 1883 Mr. G. C. Stone began a series of contributions on the "Determination of Manganese in Spiegel."[2] In his first paper he reported thirteen determinations by five chemists, all working upon the same "works" sample, showing from 15.49 to 13.83 per cent., and also twenty-six determinations by ten chemists, all working upon a sample of the same spiegel, prepared with especial care jointly by Mr. Stone and one of the other chemists, showing from 14.56 to 10.36 per cent. But some of the low results were obtained by experimental methods.

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[1] Trans. A. I. M. E., 15, 104.

[2] Trans. A. I. M. E., 11, 323 : 12, 295 and 514.

In the fall of 1883 Mr. Stone reported twenty additional determinations by five other chemists, ranging from 14.20 to 10.76 per cent.; the extremes being reported by the same chemist when working by different methods, his favorite method giving from 13.84 to 13.65 per cent., and three low results, less than eleven per cent., being obtained by the Williams' method. In this connection Mr. Stone presented an interesting table, dividing the methods used into four classes and the results into three classes, giving respectively, below thirteen per cent., between thirteen and fourteen per cent., and above fourteen per cent.

In the spring of 1884 Mr. Stone reported twenty-seven new results, nineteen by four new chemists, and eight by one previously reported, whose new results were obtained by several methods.

We have thus seventy-three determinations by nineteen different chemists. Of these two are thrown out on account of the method used, and eleven "because the chemists were not entirely satisfied with them," leaving sixty determinations by eighteen chemists, using twelve methods.

These sixty results range from 14.47 to 12.60 per cent., and average 13.39 per cent. Leaving out eight determinations by one method which is considered to give low results, the lowest determination becomes 12.92 per cent. and the average 13.48 per cent., showing an extreme variation of 1.45 per cent. of manganese between the highest and lowest results, and showing only forty-four per cent. of the results within two-tenths per cent. of the average.

In the discussion of Mr. Stone's second paper, Mr. J. B. Mackintosh[1] presented an analysis of Mr. Stone's first forty-six results, retaining the results by the Williams' method, from which he argued that the evidence pointed to 12.956 per cent. as the true content of manganese in this spiegel. If this is the case, then there is a very decided tendency to get too high results in this class of work.

Taken as a whole, this investigation would seem to show that variations of five-tenths per cent. in the determination of manganese in this grade (ten to fifteen per cent. manganese) of

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[1] Trans. A. I. M. E., 12, 300.

spiegel are to be expected, and much wider variations may be found.

PHOSPHORUS IN PIG IRON.

Early in the 80's, Messrs. Potter and Riggs, of St. Louis, Mo., sent out a sample of pig-iron for the determination of phosphorus.

This examination yielded twenty-six results, by eleven chemists, using five methods, ranging from 0.181 to 0.141 per cent., and averaging 0.160 per cent. and showing an extreme variation of 0.040 per cent. The maximum variation reported by any one chemist was 0.017 per cent., while three reported duplicates agreeing with 0.001 per cent. These results have never been published. One of the chemists discovered arsenic in the sample, which would account for some of the variation in the series. His determinations in duplicate were 0.151 and 0.152 per cent.

In February, 1882, Mr. F. E. Bachman presented a paper to the American Institute of Mining Engineers,[1] in which he reported forty-four results by eighteen chemists, using four methods, ranging from 0.165 to 0.096 per cent. and averaging 0.143 per cent. The extreme variation was 0.069 per cent. The maximum variation reported by any one chemist on straight duplicates was 0.01 per cent., and the minimum 0.0004 per cent. Experimental determinations by Mr. Bachman, using different processes, yielded variations amounting to 0.043 per cent.

At the Atlanta meeting in October, 1895, Mr. Geo. Thackray presented a paper, entitled "A Comparison of Recent Phosphorus Determinations in Steel."[2] He first gives a table of determinations of phosphorus by two chemists on eight samples ranging from 0.033 to 0.012 per cent., one chemist uniformly getting high results. One chemist found from 0.080 to 0.074 per cent., and the other 0.116 to 0.088 per cent in these steels. These results were manifestly unsatisfactory.

A second table shows results by three chemists, the buyer's, the seller's and an arbitrator. By the arbitrator's determinations these steels carried from 0.080 to 0.063 per cent. of phosphorus.

[1] Trans. A. I. M. E., 10, 322.

[2] Trans. A. I. M. E., 25, 370.

The maximum difference in any set of three results was 0.017 per cent., and the minimum 0.005 per cent.

These results were obtained in the settlement of sales. As a result of the discussion which accompanied the matter, two samples of steel were prepared and sent to various chemists. A fourth table gives thirty-six results obtained from twenty-three chemists, using twenty-nine methods on one steel, showing results averaging 0.0496 per cent., and ranging from 0.055 to 0.045 per cent., an extreme variation of only 0.010 per cent. Any individual result was practically within 0.005 per cent. of the average.

On the second sample thirty-eight results were reported averaging 0.0835 per cent., and ranging from 0.091 to 0.076 per cent., an extreme variation of 0.015 per cent.

My own results on these steels are not given, as they were not reported in time; but they add two more results by one more chemist in each case, and the results fall within the limits.

These results must be regarded as highly satisfactory, and show that here, at least, is one determination that can be made by many chemists, working in different ways, and yet with results agreeing very closely together. While it may not be necessary to determine many things as closely as phosphorus in steel, yet it would be highly satisfactory if we could do so; and this is a good standard of excellence for us to aim at.

PHOSPHORIC ACID.

As compared with the accuracy secured in the determination of phosphorus in steel, the 1894 report of the Association of Official Agricultural Chemists,[1] shows that on one sample thirty-nine determinations of insoluble phosphoric acid by eighteen chemists, working by the official method, showed results ranging from 0.45 to 0.03 per cent., with an average of 0.27 per cent., the extreme variation being 0.42 per cent., or over one and one-half times the average determination.

By another method, on the same sample, thirty-six determinations by nineteen chemists showed results varying from 0.34 to

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[1] Proceedings of the Eleventh Annual Convention of the Association of Official Agricultural Chemists, August 23, 24, 25, 1894. Bulletin 43, U. S. Department of Agriculture, Division of Chemistry, p. 76.

0.04 per cent., with an average of 0.19 per cent., the extreme variation being 0.30 per cent., or over one and one-half times the average.

We have thus seventy-five determinations by nineteen chemists working by two methods, showing results ranging from 0.45 to 0.03 per cent., with an average of 0.233 per cent., the extreme variation being 0.42 per cent., or nearly twice the average determination.

On another sample thirty-three determinations by seventeen chemists working by the official method, showed results ranging from 3.85 to 2.24 per cent., with an average of 2.82 per cent., the extreme variation being 1.61 per cent., or considerably more than one-half of the average.

By another method, on the same sample, thirty-five determinations by seventeen chemists showed results ranging from 3.49 to 2.18 per cent., with an average of 2.83 per cent., the extreme variation being 1.31 per cent., or nearly one-half the average.

Summing up again, we have sixty-eight determinations by eighteen chemists working by two methods, showing results ranging from 3.85 to 2.18 per cent., with an average of 2.82 per cent., the extreme variation being 1.67 per cent.

The same report[1] shows that on one sample the results of twenty-nine determinations of citrate soluble phosphoric acid by fourteen chemists, by the direct method of Ross, varied from 2.47 to 1.04 per cent., with an average of 1.52 per cent., the extreme variation being 1.43 per cent., or nearly equal to the average of all the determinations.

On the same sample, by the official method, the results of twenty-three determinations by fourteen chemists ranged from 2.26 to 1.18 per cent., with an average of 1.46 per cent., the extreme variation being 1.08 per cent., or over two-thirds of the average determination.

Summing up, we have fifty-two determinations by fourteen chemists working by two methods, ranging from 2.47 to 1.04 per cent., and averaging 1.49 per cent., the extreme variation being 1.43 per cent., or nearly equal to the average.

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[1] *Ibid.*, p. 72.

On another sample thirty-six determinations by fifteen chemists by the direct method of Ross, range from 3.29 to 1.87 per cent., with an average of 2.36 per cent., the extreme variation being 1.42 per cent., or considerably over one-half of the average determination.

On the same sample, twenty-four determinations by fifteen chemists, ranged from 3.40 to 2.08 per cent., with an average of 2.60 per cent., the extreme variation being 1.32 per cent., or a little over one-half of the average determination.

Summing up, we have sixty determinations by fifteen chemists working by two methods, ranging from 3.40 to 2.08 per cent., and averaging 2.44 per cent., the extreme variation being 1.32 per cent., or a little over one-half of the average determinations.

In the determination of the total phosphoric acid,[1] forty-five determinations, by eighteen chemists, ranged from 20.67 to 19.74 per cent., with an average of 20.09 per cent., the extreme variation being 0.93 per cent. By a volumetric method, thirty determinations, by eleven chemists, ranged from 20.60 to 19.83 per cent., with an average of 20.14 per cent., the extreme variation being 0.77 per cent. By another volumetric method, twenty-one determinations by ten chemists, ranged from 20.45 to 19.27 per cent., with an average of 19.96 per cent., the extreme variation being 1.18 per cent.

Combining these results, we have ninety-six determinations by eighteen chemists working by three methods, ranging from 20.67 to 19.27 per cent., with an average of 20.08 per cent., the extreme variation being 1.40 per cent.

Similarly, on another sample, we have 120 determinations, by twenty-two chemists, working by the same three methods, ranging from 18.15 to 16.25 per cent., with an average of 17.26 per cent., the extreme variation being 1.90.

Again, on another sample, we have ninety-six determinations by twenty-one chemists, working by the same three methods, ranging from 2.85 to 2.20 per cent., with an average of 2.50 per cent., the extreme variation being 0.65 per cent.

COPPER.

At the August meeting of the A. I. M. E., in 1882, Mr. W.

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[1] *Ibid.*, pp. 81, 82, 83.

E. C. Eustis presented a paper entitled "Comparison of Various Methods of Copper Analysis."[1] For the purpose of this comparison a very complex sample was made up, containing sulphides, oxides and metallic copper, a silicate, sulphides of iron and zinc, arsenic and nickel. The paper reports forty-five determinations by seventeen chemists, using some eight methods. The results showed a wide variation, ranging from 53.34 to 43.92 per cent. and averaging 47.75 per cent. On throwing out a set of six results from one concern, all of which were more than two per cent. and two of them nearly five per cent. above the nearest other result, as being manifestly too high, and two results by one chemist and one method, which were more than two per cent. below the nearest other result, the series still ranges from 48.72 to 46.24 per cent., with an average of 47.23 per cent., and a maximum variation of 2.48 per cent., which cannot be considered very satisfactory.

The same paper reported seventeen determinations by seven chemists on borings of pig copper. These ranged from 91.07 to 98.17 per cent. and averaged 94.25 per cent. On throwing out two results that were nearly three per cent. higher than the nearest other result, and four that were over three per cent. below the nearest other result, the series ranges from 94.91 to 94.38 per cent. with an average of 94.69 per cent. The extreme variation of only 0.53 per cent. must be regarded as very good work, especially when we consider the character of the material.

At the Florida meeting in March, 1895, the results of a symposium on copper and copper matte, initiated by Dr. A. R. Ledoux, of New York City, were presented.[2] Eight chemists reported the copper in the matte, some in duplicate or more, as determined by electrolysis, as ranging from 55.17 to 54.50 per cent. and averaging 54.91 per cent. The extreme variation was only 0.67 per cent; and this must be regarded as satisfactory, and very much better than the results on Mr. Eustis complex mixture.

Six chemists reported results by the cyanide method, ranging from 54.8 to 50.55 per cent. all but one of the results being below

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[1] Trans. A. I. M. E., 11, 120.

[2] Trans. A. I. M. E., 25, 250 and 1000.

the lowest electrolytic result. These cannot be regarded as satisfactory.

A plate of copper made from melted anodes was drilled and six chemists reported the copper in the drillings, as found by the electrolytic method, as ranging from 98.46 to 97.04 per cent., and averaging 97.67 per cent. with a maximum difference of 1.42 per cent. These results are not as good as those previously reported by Mr. Eustis.

GOLD AND SILVER IN COPPER MATERIALS.

The symposium above referred to was undertaken primarily to test methods of assaying copper material for gold and silver. Fourteen chemists reported the silver by scorification assay, some entirely uncorrected, some partially corrected, and some corrected for both loss in slag and cupel and presence of copper in the silver button. The averaged results ranged from 135.38 to 122.88 ounces per ton and averaged 128.86 ounces per ton; the extreme variation being 12.5 ounces per ton, or nine and seven-tenths per cent. of the average.

Nine chemists reported ten results by combined wet and scorification methods, a few of them corrected for slag and cupel absorption. The averaged results ranged from 130.68 to 123.03 and averaged 127.25 ounces per ton. The extreme variation was seven and six-tenths ounces per ton, or 5.97 per cent. of the average determination.

One chemist reported 123.6 ounces per ton by crucible method.

Another reported 126.2 ounces per ton by combined wet and crucible method, corrected for slag and cupel.

Summing up, we have twenty-six results by twenty chemists working by two main methods, but both of them modified in various ways, and two methods, each by a single chemist, varying from 135.38 to 122.88 and averaging 127.94 ounces per ton. The extreme variation was 12.5 ounces per ton, or 9.77 per cent. of the average determination.

In the case of the silver assay of the copper borings, nine chemists reported by the scorification method, with and without corrections. The averaged results varied from 164.35 to 154.40, and averaged 159.36 ounces per ton. The extreme variation was 9.95 ounces per ton, or 6.24 per cent. of the average.

Fifteen chemists reported sixteen results by combined wet and scorification methods, with and without corrections. The averaged results varied from 161.40 to 148.50 and averaged 156.48 ounces per ton. The extreme variation was 13.9 ounces per ton, or 8.88 per cent. of the average. A single chemist reported 161.35 ounces per ton by combined wet and crucible process, corrected for slag and cupel.

Summing up, we have twenty-six determinations by twenty chemists working by three methods, ranging from 164.35 to 148.5 and averaging 157.67 ounces per ton. The extreme variation was 15.85 ounces per ton, or 10.05 per cent. of the average determination.

Twenty chemists working by the four methods reported twenty-six results on the gold in the matte varying from 2.41 to 1.85 and averaging 2.245 ounces per ton. The extreme variation was 0.56 ounce per ton, or 24.94 per cent. of the average.

On the gold in the copper borings twenty chemists working by two main methods, each one variously modified, and the combined wet and crucible method by a single chemist, reported twenty-six results varying from 0.501 to 0.205 and averaging 0.307 ounce per ton. The extreme variation was 0.296 ounce per ton, or 96.4 per cent. of the average determination.

POTASH.

In the determination of potash the 1894 report of the Association of Official Agricultural Chemists[1] gives six determinations of potassium chloride by six chemists by one method, ranging from 97.79 to 99.32 per cent. with an average of 98.56 per cent, the extreme variation being 1.53 per cent. By another method on the same sample seven determinations by seven chemists range from 97.21 to 98.86 per cent., averaging 98.16 per cent. Combining these results we have thirteen results by seven chemists, by two methods, ranging from 97.21 to 99.32 per cent. and averaging 98.35 per cent., the extreme variation being 2.11 per cent.

This report contains also a table of results on soil analyses[2] which I quote entire.

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[1] page 22.

[2] page 41.

TABLE OF AVERAGES.

Soil Sample No. 2.

	Provisional method.					Hilgard method.				
	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.
		Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	Per cent.	
Insoluble matter	14	76·874	77·733	76·19	2	12	76·619	77·910	75·380	3·3
K_2O	13	0·405	0·510	0·27	59	11	0·431	0·670	0·250	98
CaO	13	0·460	0·605	0·360	53	10	0·538	0·680	0·390	54
MgO	11	0·425	0·589	0·360	54	9	0·425	0·627	0·320	72
Fe_2O_3	9	3·504	4·260	2·955	37	7	4·347	6·400	3·300	70
Al_2O_3	9	6·613	7·500	6·240	19	7	6·285	6·828	4·460	38
P_2O_5	16	0·496	0·600	0·410	38	12	0·510	0·660	0·430	45
Fe_2O_3, Al_2O_3, and P_2O_5	12	10·754	11·400	10·220	11	10	11·071	12·100	10·550	14
N	7	0·276	0·290	0·262	10	..	.....	.....	.....	....
P_2O_5, Goss method	5	0·467	0·493	0·425	15	..	.....	.....	.....	....

Soil Sample No. 3.

	Provisional method.					Hilgard method.				
	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.
		Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	Per cent.	
Insoluble matter	11	80·520	81·255	79·980	1·6	10	80·448	82·010	79·47	3·1
K_2O	10	0·422	0·500	0·305	46	9	0·396	0·630	0·240	98
CaO	9	0·372	0·425	0·300	33	8	0·411	0·600	0·275	79
MgO	8	0·381	0·524	0·270	67	7	0·369	0·490	0·265	61
Fe_2O_3	6	3·251	4·330	2·310	62	5	3·746	4·870	3·025	49
Al_2O_3	6	6·191	7·440	5·670	29	5	5·770	6·164	5·050	19
P_2O_5	11	0·418	0·555	0·350	49	9	0·429	0·560	0·309	59
Fe_2O_3, Al_2O_3, and P_2O_5	8	9·927	10·350	9·440	9	7	10·091	10·590	9·550	10
N	6	0·190	0·224	0·175	26	..	.....	.....	.....	....
P_2O_5, Goss method	4	0·369	0·390	0·354	10	..	.....	.....	.....	....

REVIEW

ON THE DEVELOPMENT OF SMOKELESS POWDER.[1]

BY CHARLES E. MUNROE.

To intelligently present a sketch of what has been done in the development of smokeless powder, it is necessary to first briefly review the history of black gunpowder. Although the place and date of its origin and the name of its inventor are yet open to dispute, it is generally accepted that it was employed as a propellent in cannon at the battle of Crécy in 1346, and in small arms for some time prior to this date, and that it then consisted of a mixture of niter, charcoal and sulphur. Considering the existing state of chemistry, it is fair to infer that the making of gunpowder, like the manufacture of guns, was for long an empiric art, and that, notwithstanding that Tartaglia, Galileo, Newton, Huygens, and many others speculated upon and discussed the effects which gunpowder produced upon projectiles; that granulating was employed in 1445; that Cellini had observed the necessity of adapting the grains to the piece; that sizing was practised in France in 1525, and that Hawksbee had in 1702 measured the volume of gas resulting from a known volume of gunpowder, the science of gunnery had no existence until Robins devised the ballistic pendulum by which he measured the velocity of projectiles and with which he obtained the experimental data upon which his "New Principles of Gunnery," printed in 1742, was founded. The science of exterior ballistic was materially improved when Hutton, in 1778, extended Robins' principle to the use of the gun as the pendulum also, for it became then possible to not only measure the velocity of the projectile, but the energy involved in the reaction, and this method was employed for larger and larger calibers until it reached its practical limit in the very elaborate and precise series of experiments made at the arsenal in this city (Washington) from 1842 to 1847, by Major Mordecai, who succeeded in swinging cannon weighing about 7,700 pounds and throwing 32-pound balls; but this necessitated the use of a pendulum weighing over 9,300 pounds, the center of gravity of which was over fourteen feet below the axis of suspension. The weight and length of the pendulum increases so rapidly with the increase of the projectile that to determine by this method the velocity of the projectile from a 100-ton gun, would require towers like those from which the Brooklyn bridge is suspended, between which to swing the pendulum.

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[1] Presidential address delivered before the Washington Section of the American Chemical Society, Feb. 21, 1896.

Opportunely as this limit was approached, Dr. Joseph Henry announced, in 1843, his invention of a method for the determination of velocities by interposing screens, which were electrically connected with chronographs, in the path of a projectile and at definitely determined distances from the gun, and this method, which while possessing the merit of great simplicity, is at the same time very precise and capable of being used for determining the velocities of projectiles from guns of every calibre, is now universally employed with chronographs, such as the Boulengé, Schultz-Deprez, and Mahieu, while the principle has been extended by Captain Noble to the study of interior ballistics, in his very ingenious chronoscope by which the velocity of the projectile can be determined at frequent intervals, even when it is moving through the bore of the gun.

The ability to measure the velocities which it produced led to active investigations into the properties of gunpowder and resulted in the experiments of Lavoisier, between 1777 and 1778 on the deflagration of powder, of Berthollet, on the best proportions for mixing the ingredients, of Gay Lussac, on the refining of niter, of Violette, on the production, composition and properties of charcoal, of Gay Lussac and Chevreul, of Bunsen and Schischkoff, of Linck, and of Károyli, on the composition and volume of the products of the combustion of this substance, and of many other experimenters on the effects resulting from differences in the density, hardness, size of grain and other physical characteristics of the explosive. But notwithstanding the great advance made through the invention of methods by which to measure the velocity of the projectile and the recoil of the piece, the science of gunnery was still incomplete without an accurate knowledge of what was going on within the chamber and particularly what pressures were produced and how this pressure was distributed within the gun before the projectile left its seat and while it was traveling through the chase; yet, although direct experimental determinations of the pressure exerted by fired gunpowder were made by Count Rumford in 1797 in a somewhat rude device, and numerous indirect estimations were deduced from the observations of Robins on the volume of the gases produced by its combustion and from the more precise and detailed researches of Bunsen and Schischkoff and the other experimenters previously referred to, no practical means were at command by which to make direct measurements of the pressure developed within the gun itself until Captain Rodman, in 1857, invented the pressure gauge, described in his "Reports of Experiments," published in Boston, in 1861, which in common with several modifications of it, such as the Noble crusher gauge and the Woodbridge spiral gauge, came into general use in all experimental firing and in the proving of guns and powders.

In estimating the pressure developed by powder from the data obtained in their chemical analyses of its products, Bunsen and Schischkoff proceeded on the assumption that Piobert's conclusion from his experiments, *viz.*, "that the rate of combustion of powder is not affected to any sensible degree by heat or pressure," was correct; but their conclusions having been questioned by many authorities, among them by Vignotti, in 1861, and by Craig about the same time, who showed that the products of combustion differs with the pressure, and their physical data by F. A. P. Barnard, who submitted them to a reinvestigation in 1863, and arrived at a widely different result; and they having also failed of verification by the pressure gauge, the matter was again experimentally attacked by Noble and Abel, who employed as a firing chamber a hermetically closed steel cylinder sufficiently strong to resist rupture by the explosion of a charge of powder which completely filled it (such as Dr. Woodbridge had previously used at the Washington navy yard in 1856), in which pressure gauges were enclosed, and they fired the charge by the electric method invented by Dr. Robert Hare in 1832. In addition the apparatus was so contrived that the gaseous and solid products could be collected, measured and analyzed at will.

With this they found that when powder is fired in a confined space the products of combustion are about fifty-seven per cent. by weight of ultimately solid matter, and forty-three of gases, which at 0° C. and 760 mm., occupy about 280 times the volume of the original powder. That the temperature of explosion is about 2,200° C., and the tension of the products, when the powder entirely fills the space in which it is fired, is about 6,400 atmospheres, or forty-two tons per square inch.

When fired in the bore of the gun it was shown that the work on the projectile is effected by the elastic force resident in the permanent gases, but the reduction of temperature, due to the expansion of the permanent gases, is in a great measure compensated for by the heat stored up in the liquid residue. The total theoretical work of gunpowder when expanded indefinitely (as for instance in a gun of infinite length) was deduced from the data which they accumulated as about 486 foot tons per pound of powder.

They further ascertained that the fine grain powders furnish decidedly smaller portions of gaseous products than large grain or cannon powders; that the variations in the composition of the products of explosion, in a closed vessel, furnished by one and the same powder, under different conditions as regards pressure. and by two powders of similar composition, under the same conditions of pressure, are so considerable that no chemical expression can be given for the metamorphosis of a gunpowder of a normal composition, and that the proportions of the several constituents of the solid residue are quite as much affected by slight accidental conditions of explosion of one and the same powder in different experiments as by decided differences in the composition or in the size of the grain.

The subsequent researches of Berthelot and Vieille, and of Sarrau and Vieille showed that gunpowder was not singular in that its combustion products varied with the variations in the conditions prevailing in the firing chamber, but that this same rule held for gun cotton, picrates and other explosives, also, and that consequently the chemical reaction taking place and the physical phenomena attending them were changed with these varying conditions, and more particularly with variations in the density of loading.

Before the invention of the instruments of precision above alluded to, guns were constructed largely on principles deduced from observations of exterior phenomena, and powder was manufactured largely by rule of thumb. With the ability to determine quantitatively their behavior, each has been studied in a scientific manner and improved by rational methods.

By their use the real importance of uniformity in chemical and physical composition was demonstrated for the powder, and the means by which to "prove powder" before issue were supplied, while rational blending, by which to minimize the irregularities incident to the best commercial processes was made possible. At the same time greater uniformity in granulation was secured; the best form of grain was developed for great guns through the pebble to the mammoth, disk, pellet, sphere, cylinder, hollow cylinder, hexagon and cube to the hexagonal prism, with one canal, which is now generally adopted, and which is a modified form of the grain invented by Rodman; the size of the grain best adapted for a given gun was ascertained, and the size rose trom one-sixth of an inch, as used in the 15-inch S. B., to fhe hexagonal prism one inch in height by 1.36 inches in diameter; the density of the grain rose from 1.60 to 1.86; the effect of prearranged variations of density in grains, as proposed by Doremus and carried out in the Fossano powder, was determined; and the important part which moisture played in the reactions going on in the chamber with the necessity for introducing it into the grain in definite quantities and retaining it there within very narrow limits was discovered. In fact these methods of inspection have become so precise and the powder specifications so severe that the manufacture of military gunpowder is now a most difficult art, and the maker must not only watch the barometer and thermometer and hygrometer to determine his action at each step of his process, but according to one authority, he must "vary his treatment with each passing cloud," and notwithstanding all precautions, it is no uncommon thing for the best makers to have their product rejected at the proving ground.

Besides these improvements in black gunpowder, which have resulted from our ability to accurately gauge its performance, these instruments have shown us that it is possible to avail ourselves of the energy stored up in underburned charcoal or carbohydrates if we but modify the brusqueness incident to mixtures containing them by adopting the proper size, form, hardness and density for the grain, and this has resulted in the cocoa or brown prismatic powders which have come into very extented use since 1880.

The valuable properties of the compressed powder were then applied for use in small calibers and enabled Hebler to realize a marked increase in efficiency for his rifles, and in these forms the limit of efficiency of gunpowder appeared to be reached.

But while this was being accomplished, progress was being rapidly made along other lines which we will briefly point out.

Among the other inventions in gunnery which preceded the invention of smokeless powder, and made its use possible or essential, we may mention the introduction of rifling, by which greater accuracy of fire and a higher velocity and penetrating effect is obtained, and which, while invented by Gaspard Zollner, of Vienna, in 1480, did not come into vogue until 1830, or general use until much later. Breech loading, which was known among the Chinese as early as 1313, but which has practically been developed since 1863, our civil war having been fought chiefly with muzzle loaders. Percussion caps, invented by Joseph Egg, in 1818, and adopted, with the nipple, in France in 1838. Self obturating metallic ammunition, which depended on the preceding invention, and which we owe apparently to Flobert, who introduced it for use, with a quick powder, in his parlor rifle in 1845, though it did not come into use for larger caliber for some years later, and then only after the discovery of a metal having the necessary ductility and strength from which to strike the shells and the perfecting of machinery for their economic and rapid production. Magazine rifles and machine guns, the earlier practical forms of the latter being the weapon exhibited by Dr. Gatling in 1867, and the French mitrailleuse, and which have now developed into the automatic machine guns, such as Maxim, Colt, Hotchkiss, and others possessing an almost incredible rapidity of discharge. Rapid fire large caliber guns, which, like the foregoing, depend for their development on the prior invention of the breech mechanism, and the metallic ammunition and which have reached calibers of six-inch diameter and throw 100-pound shot at the rate of six per minute, with a velocity of over 2,000 feet per second. Breech-loading, built-up steel rifles, which, while embodying the ideas of a gun of equal strength, as announced by Professor Treadwell, in 1843, the mechanical devices of Chambers patented in 1849, and the principles of initial tension, as expounded in Rodman's publication of the same year, have been developed, at least in this country, only since the appointment of the Gun Foundry Board by Secretary Chandler, and whose manufacture was then rendered possible only through the perfection which our machine tools had attained and the improvements achieved in the metallurgy of steel. Small caliber rifles, with steel or german-silver mantled bullets, which are sighted for about two miles, and whose projectile will pierce six men, standing one behind the other in close order, at 1,000 yards. And finally to the invention of range-finders or telemeters, through which by trigonometric or mechanical methods, the position of the far distant targets now in range of new weapons may be located with precision.

For it is evident that to use these precise and powerful weapons and instruments, with the accuracy and rapidity they are capable of, the atmosphere must remain clear, and the piece must remain clean, while at the same time the highest attainable velocity must be imparted to the projectile without an undue strain being brought upon the gun. Yet we have seen that Noble and Abel found that military gunpowder gives off, on combustion, fifty-seven per cent. by weight of ultimately solid matter which is either thrown into the atmosphere to produce smoke or left as a residue to foul the bore. How considerable this smoke producing capacity of gunpowder is may be estimated if we take a Gatling firing 1200 rounds of small arm ammunition per minute (and this by no means expresses the highest attainable speed to-day) and assume that all the solid matter is driven out the gun, when we shall find that each minute six and six-tenth pounds of finely divided solid matter will be projected into the atmosphere. Add to this, in a general engagement, the smoke from the great guns, which, as with the 110-ton gun, can project 528 pounds of this solid product at each discharge, and that coming from the rapid fire, and magazine rifles, and it is obvious that unless a favorable breeze is blowing or other favorable atmospheric conditions prevail, the force or ship will soon be enveloped in an opaque cloud of smoke and be at the mercy of an invisible foe. It is, I repeat, conditions such as these which have rendered smokeless powder, of good ballistic qualities, a great desideration, if not an absolute necessity.

While the development of the projectile, the musket, the machine gun, and ordnance; the perfection in the compositions, forms, and manufacture of gunpowder; and the invention of the instruments and devices for gauging and controlling their performance was going on, chemists were engaged in adding their contributions to the fund of human knowledge in the field of explosives. In 1788 Hausmann discovered "picric acid," in 1800 Howard discovered mercuric fulminate, in 1845 Schönbein discovered gun cotton, in 1845 Sobrero discovered nitroglycerin, in 1875 Nobel invented explosive gelatine, and in the meantime, or subsequently, numerous allied nitro-substitution compounds, nitric ethers and diazo-bodies, less generally known than those above enumerated, were produced, and identified, and shown to possess explosive properties.

The earlier experimental tests of these bodies proved that not only were some of them more powerful or more violent explosives than gunpowder, but that no smoke accompanied their explosion, since the products of their explosive decomposition were gases or vapors at the prevailing temperatures and efforts were put forth soon after their discovery to adapt them for use as propellents. These, together with various organic solids, and liquids to serve as solvents and hardening agents and ammonium and barium nitrates to serve as oxidizing agents were known and at hand.

The earliest experiment with smokeless powder was probably that made by Howard, in 1800, when he tested the properties of his newly discovered mercuric fulminate and found that though this violent agent produced little smoke, imparted a low velocity to the projectile and but a slight recoil to the piece, it burst the chamber, and demonstrated its unfitness to compete with gunpowder as a ballistic agent. Nevertheless this substance has since found a limited use, when mixed with solid diluents which act as restrainers, in ammunition for parlor rifles, and it is noticeable that when firing this ammunition there is little smoke and a scarcely audible report attending the discharge.

In 1806 Grindel carried out a somewhat extended series of experiments with a view to substituting ammonium nitrate for potassium nitrate as the oxidizing agent in gunpowder mixtures but the deliquescent character of the ammonium salt rendered the powder made with it useless under the then existing conditions, and has proven a formidable obstacle to its use in many of the attempts subsequently made. The fact, however, that the products of its combustion, at the prevailing temperature, are wholly gaseous rendered it a tempting material to inventors of smokeless powders and it has been more recently used, among others, by F. Gaens, who, in 1885, patented, in Germany, his so-called "Amide Powder," produced by mixing eighty parts of ammonium nitrate and 101 parts of potassium nitrate, with forty parts of charcoal. He claimed that this mixture was not hygroscopic and was practically smokeless, and he held that by the reaction consequent on the ignition, a potassamine was formed which was both volatile and explosive. Whatever the nature of the reaction, it appears from the reports that an ammonium nitrate powder was produced about this time in Germany and later in England, under the name of Chilworth Special, which possessed remarkable ballistic properties and yielded comparatively little smoke, which speedily dispersed, and which bore exposure very well until the humidity of the atmosphere approached saturation.

It is possible that the ammonium nitrate used may have been produced by Benker's process, in which the salt is formed by metathesis from solutions of sodium nitrate and ammonium sulphate exposed to a temperature of —15°, or below, for it is claimed that the ammonium nitrate which crystallizes out under these circumstances is of extraordinary purity and not at all hygroscopic.

It would appear that though these ammonium nitrate powders are slightly hygroscopic, they may retain their good qualities for long times in the hermetically sealed cases used in fixed ammunition up to the six-inch rapid fire gun, but that we know that the small amount of water necessarily present produces marked changes during long periods of storage with varying temperatures and that the ammoniacal salts attack the copper of the shells. Besides, too, we must remember that ammonium nitrate in common with other ammonium salts gives off ammonia, when heated or exposed to the air, and becomes acid so that we are debarred from using it in the presence of any bodies affected by the acid.

The next step toward the development of our modern smokeless powder was taken when, soon after the discovery of guncotton, in 1845, attempts were made to use this material as a propellent. These experiments were made in Germany, France, and England, and a very extended series were carried on by

Major Mordecai, at the Washington Arsenal, but the material, owing to its form and the imperfection in its manufacture, proved too brisant and too irregular in its action, and so unstable on keeping as to undergo decomposition in storage. The material having been proved to possess many valuable qualities was not wholly abandoned, but it continued to be the subject of study by many chemists until in 1862, it seeming that Baron von Lenck had so perfected the methods for its manufacture and purification as to ensure stability and uniformity of composition. Austria adopted it as a propellent and supplied thirty howitzer batteries with guncotton cartridges.

This is the first instance in which a really smokeless powder was employed on any but an experimental scale and this powder foreshadowed in its composition and many of its characteristics, the best modern powders of the smokeless class. The guncotton as then made retained the fibrous condition of the original cotton and in the Austrian cartridges it was spun into thread and woven into circular webs like lamp wicks, or braided, or wound on wooden or paper bobbins, and so arranged in the piece as to secure the desired air spacing as well as to insure ignition from the front. As thus used, it was claimed to be uninjured by dampness; to require a charge of but one-fourth to one-third of that of the powder previously employed; to be capable of being regulated so as to produce widely varying effects at will; to leave no residue to foul the piece; and to produce no smoke, while the gases evolved were less injurious to both the piece and men serving it than those of gunpowder. At the same time it produced less heating effect on the gun.

Unfortunately, about this time, the factory at Hirtenberg, where the guncotton was made, blew up for some undiscovered cause, and accidents having occurred with the guns, the use of guncotton was abandoned by the Austrians.

Its fate seemed now to be sealed, but such was not the case, for the scene of action then passed to England, where Abel not long after succeeded in effecting a more complete purification of the body by pulping it prior to the final washing processes, thus cutting the tubular fiber into short lengths and rendering it possible to remove the last traces of acid retained within the tubes by capillarity and which had been the occasion of its decomposition with time. Having thus obtained his pulped, purified guncotton he compressed it into such forms as was desired, and in 1867 and 1868 he obtained with it some very promising results when used with field guns. But although comparatively small charges often gave high velocities of projection without any indications of injury to the gun, the uniform fulfillment of the conditions essential to safety proved then to be beyond control, and the military authorities not being, at that time, alive to the advantages that might accrue from the employment of a smokeless explosive in artillery, experiments were discontinued not to be resumed for nearly twenty years, and use was found for compressed guncotton in military and naval mining and especially in filling torpedoes, where it has been found the most efficient and satisfactory explosive thus far applied to this purpose.

But sportsmen, to meet whose wants and wishes many noteworthy improvements have been made in the arts, did appreciate the value, to marksmen, of smokelessness combined with high velocities and absence of fouling, and the progress made during the succeeding twenty years in the adaptation of organic nitrates to use as propellents was under their patronage and in response to their demands, and naturally, the first object sought was to so restrain the violence of the explosive that rupturing explosions, such as had occurred, could not be induced under the conditions in which the powder was to be used.

One of the first to realize a considerable degree of success was Captain Schultze, of the German artillery, who made a powder from well purified and partly nitrated wood. For this purpose he sawed the wood into sheets about one-sixteenth of an inch in thickness, which were passed through a machine that punched out discs or grains of uniform size. The grains were then deprived of their resinous matter by being boiled in sodium carbonate, washed, steamed, and then bleached with chloride of lime, when finally, after drying, the cellulose was nitrated in an acid mixture, such as is used for making guncotton. The nitrated wood was then steeped in a solution of potassium and barium nitrates, and when dry the powder was finished. By this means a nitrocellulose was produced which was diluted with unconverted cellulose and metallic nitrates, which were so intimately mingled that a fairly even rate of combustion was obtained though abnormal results were not wholly avoided.

The advantage of using nitrates and combustible organic substances as diluents was soon recognized ; and, as a consequence, many powders of this nature were devised, some thirty of them having been produced and many of these put on the market, in which we find that potassium, sodium and barium nitrates, and potassium chlorate were used as oxidizing agents and sugar, cellulose, charcoal, sulphur, starch, dextrin, gums, resins, and paraffine as combustible diluents and cementing agents. All, however, approximated black gunpowder, as regards physical structure and none attained to complete success as regards uniformity of fire and reliability of pressure.

In 1882 Messrs. Reid and Johnson patented the process for making E. C. powder, in which the pulped nitrocellulose and nitrates was agglomerated into grains by revolving the moistened mass in barrels, drying the grains, moistening with ether to harden them, and then coloring them with aurine.

About 1885 Messrs. Johnson and Borland produced the J. B. powder, in which a new idea, as regards powder manufacture, was introduced, though it had been used elsewhere for many years. The inventors mixed nitro cotton with barium nitrate and with or without charcoal or torrefied starch and granulated the mixture in a revolving drum, while the water was admitted in a fine spray. When granulated the grains were dried and then moistened with a solution of camphor in petroleum spirit, and after a time heated in a water jacketed vessel to evaporate the benzine, and the bulk of the camphor. By this treatment the grains were hardened and rendered more slowly inflamable.

As this method of treatment resembles in some particulars that followed in the production of celluloid, though it differs in details, and as several of the smokeless powders are made by methods which are adapted from this art, you will pardon me if I briefly describe it.

Celluloid is made from that form of cellulose nitrate known as nitro-cotton or soluble guncotton, and which is produced by immersing unsized and uncalendered tissue paper for a short time in a comparatively weak acid, both being kept at a moderately high temperature. This nitro-cotton is pulped in a rag engine, dried and moistened with camphor spirits. If a considerable portion of camphor spirits be added, and the mixture be allowed to stand for awhile, the mass becomes converted into a soft translucent amber gum; with more of the spirit the nitro-cotton will be completely dissolved; but as carried out, the proportion of spirit added is insufficient to produce a very apparent change.

The mixture is now taken to incorporating rolls or "grinders," (as they are called in the caoutchouc industry), where it is intimately mixed and well pressed; when the particles cohere and the whole becomes converted into a plastic, translucent homogeneous mass which behaves like India rubber and resembles it superficially in every particular but color. After incorporation, by cutting the length of the roll, the mass may be stripped off in one continuous, coherent sheet, which on exposure to the atmosphere, through which the spirit and camphor are volatilized, hardens to a hornlike mass.

In the manufacture of a smokeless powder by this means, it is customary to mix with the nitro-cotton or mixed cellulose nitrates, a small proportion of other nitrates in order to effect complete combustion and a restrainer to assist in bringing the rate of combustion within normal limits; and this mixing is easily effected on the incorporating rolls. Barium nitrate is the salt which is perhaps most largely used, and it is preferred because it is very permanent, contains a fair proportion of available oxygen which it yields with comparative readiness, and possibly because the carbonate which is formed by the combustion has so high a specific gravity that it settles with considerable speed.

Other solvents besides camphor spirits are employed when the higher cellulose nitrates are used in the manufacture of the powder. Thus Engel takes a cellulose nitrate prepared from wood, while Glaser employs that prepared from paper or cardboard and treats it, when dry, with ethyl acetate or acetone, the action of the solvent being aided by mechanical kneading in a suitable vessel until a viscid paste or gelatinous mass is obtained with which the barium nitrate and a hydrocarbon, such as naphthalene, is incorporated. The mass is then formed into any desired shape and the solvent is allowed to evaporate or is distilled off by any suitable means when the powder is left as a dense horny material, with a glassy fracture, which can be readily granulated.

The first military smokeless powder of the modern class was made in France in 1886 by Vieille, and is said to have been compounded of cellulose nitrates mixed with picric acid, but it was soon abandoned in favor of the Poudre B., which consisted of cellulose nitrates alone, or Poudre B. N., which consisted of these nitrates mixed with barium nitrate and potassium nitrate as oxidants, and sodium carbonate as a neutralizer. Both these mixtures were condensed and hardened to a celluloid-like mass by means of a solvent like ether-alcohol, ethyl acetate or acetone.

Excellent ballistic results have been reported from France as being obtained with these powders, and they have been adopted by the French government. At the same time similar mixed cellulose nitrate powders have been produced and used in Germany, Austro-Hungary and Switzerland; the Weteren, Troisdorf and Von Förster powders being of this class. Notwithstanding that these have so long been known, our government has, with regal graciousness, recently granted a patent to two of its officers for a powder of this composition.

These are made by mixing the ingredients together with the solvent in a kneading machine of the Werner and Pfleiderer class, in batches of one to two hundred weight, until it is converted into a dough, when it is incorporated and the solvent partly driven off by putting on the grinding rolls, by which means it is also formed into continuous sheets, whose thickness is fixed by the set of the rolls. It is preferable where thick masses are desired to first roll into thin sheets so as to evaporate the solvent as completely as possible from the gelatinized mass, and then by piling the thin sheets on one another, weld them together by running them through the rolls. They are then granulated by passing them under a set of revolving circular knives which cut them first into strips and then into rectangles of the desired size and shape. These powders are dense, hard and hornlike in appearance.

Following Vieille by about two years,[1] Nobel invented ballistite, which practically is a modified explosive gelatine, differing from it only in that while the gelatine consists of ninety-three per cent. of nitroglycerin, and seven per cent. of nitro-cotton, ballastite contains about forty per cent. of nitro-cotton and one to two per cent. of anilin or diphenylamin, which is added to the nitroglycerol nitro-cotton mixture as a neutralizing agent to ensure stability. At first the solution of the gun-cotton and gelatinization of the mixture was effected by means of camphor and later by means of benzene, but it is now produced under the English patent of Lundholm and Sayer of 1889. They discovered that while dry nitro-cotton is but slightly soluble in nitroglycerin even at moderately high temperatures, when mixed with warm water and stirred up by compressed air, gelatinization sets in and solution may be completed by pressing out the water and working in the grinder. Flexible, transparent rubber-like sheets are formed, which may be cut into flakes in cutting machines of the usual type, or in pastry cutters, or may be squirted through spaghetti machines, as is done in Italy, where these cords or threads of ballistite are known as "Filite."

It is curious to note how many of the machines devised for bread making, pastry cutting and macaroni forming, have been employed in the manufacture of smokeless powder.

In 1889 Sir Frederick Abel and Professor James Dewar secured their patents on cordite, which like ballistite, contains nitroglycerin and cellulose nitrate, but whereas ballistite is made from nitro-cotton alone, cordite is made from "gun-cotton" containing from ten to twelve per cent. of nitro-cotton, to which is added a little tannin, dextrin or vaseline to serve as a restrainer. The gelatinization is effected by means of acetone,

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[1] English Patent, January 31, 1888.

the mixture being kneaded to a dough in a water-jacketed kneading machine,compacted in a mould in a preliminary press, and the mould transferred to a spaghetti machine, where the explosive is squirted into cords. As these cords issue, they are reeled on bobbins, which are placed in the drying house to drive off the acetone. When this is completed the product of ten pressings is wound from ten one-strand reels on to one ten-strand reel and then the cordite on six ten-strand reels is wound on one drum, making a cord of sixty strands, which in short lengths forms the thirty and one-half grains charge for the magazine rifle. For the higher calibers the cords are cut in lengths as they issue from the press, dried and made up into bundles. Cordite is an elastic rubber-like mass with a light to dark brown color.

Analogous to these in composition, in that they consist of nitroglycerin with cellulose nitrates, are many powders, such as amberite, Maxim's powder, Leonard's powder, P. P. G., Peyton's powder, German smokeless powder and others, and they differ in but slight particulars. Thus Curtis and André *blend different cellulose nitrates* before incorporation so as to secure a definite nitrogen content, and then cement by ether-alcohol; Maxim restrains his powder with castor oil; Leonard restrains his with lycopodium, and adds urea crystals as a neutralizer; Walke claims to make P. P. G. from a nitro-cellulose, which is not gun-cotton, and so on.

The employment of nitro substitution compounds as bases for smokeless powders has been comparatively limited. Over twenty years ago Designolle invented powders made by mixing potassium picrate, potassium nitrate and charcoal in various proportions. Borlinetto produced them from picric acid, sodium nitrate and potassium dichromate. Abel and Brugère from ammonium picrate, potassium nitrate and charcoal, and more recently Nobel from ammonium picrate, barium nitrate and charcoal. Within a few years past a powder has been manufactured in this country and put upon the market as a sporting powder, which was composed of ammonium picrate, potassium picrate, and ammonium dichromate, but I understand it has given such irregular and abnormal pressures that its manufacture has been discontinued.

While these powders may have been smoke-weak as compared with gunpowder, it is difficult to understand how, in the presence of such amounts of metallic radicles, they could have been smokeless. A powder, however, which is made by Hermann Güttler, by dissolving nitro-lignin in molten dinitro-toluene and which he calls Plastomentite, may well possess this property, and it is reported to have given good ballistic results at the Bucharest tests of 1893.

The powder called Gelbite, and invented by Dr. Stephen H. Emmens, was also smokeless. This was made by an ingenious process in which paper in strips was nitrated to a moderate degree of nitration, then fumed with ammonia to neutralize the acid, and then treated with picric acid to neutralize the ammonia and form ammonium picrate. These strips were then rolled up into rolls as charges, but as might have been foreseen from a study of the behavior of gunpowder in guns and the study of the history of gun-cotton, this powder was too brusque in action and has been abandoned.

I began my own experiments with smokeless powder manufacture in 1889. At this time the remarkable results published from France, and the announcement that that country had adopted a smokeless powder, had produced their desired strategic effect. All her rivals were seeking to be equally well equipped and were hastening to adopt a powder even before its qualities were thoroughly proven. The newspapers contained remarkable accounts of their performances and alleged descriptions of their methods of production, which while interesting as news and conveying valuable suggestions, could not be relied upon as to accuracy in details.

At the outset, being familiar with the impossibility of securing absolute uniformity and constancy of composition in physical mixtures like gunpowder, and realizing how important this feature was with our precise modern weapons, and when employing an explosive possessing great energy, I determined to attempt to produce a powder which should consist of a single substance in a state of chemical purity. This was a thing which I had not known of having been done, nor have I yet learned that any one else has attempted it. Among the bodies at command, the nitric ethers seemed most available, and of these cellulose nitrate seemed for many reasons the most promising.

There are, as you are aware, several of these nitrates (authorities differ as to the number) which differ in their action towards solvents, though all except the most highly nitrated are soluble in methyl alcohol. In the commercial production of cellulose nitrate certainly, and so far as I have observed under all circumstances, when nitrating cellulose the product is a mixture of different cellulose nitrates. Even in the perfected Abel process for making military gun-cotton, as carried out at the Royal Gun Powder Factory, at Waltham Abbey, according to Guttmann[1], the product contains as a rule, from ten to twelve per cent. of nitro-cotton.

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[1] Manufacture of Explosives, 2, 259, 1895.

Consequently I began by purifying my dried pulped military gun-cotton, which was done by extracting it with hot methyl alcohol in a continuous extractor, and when this was completed the insoluble cellulose nitrate was again exposed in the drying room. The highly nitrated cellulose was then mixed with a quantity of mono-nitro-benzene, which scarcely affected its appearance and did not alter its powdered form. The powder was then incorporated upon a grinder by which it was colloidized and converted into a dark translucent mass resembling India rubber. The sheet was now stripped off and cut up into flat grains or strips, or it was pressed through a spaghetti machine and formed into cords, either solid or perforated, of the desired dimensions, which were cut into grains. Then the granulated explosive was immersed in water, boiling under the atmospheric pressure, by which the nitro-benzene was carried off and the cellulose nitrate was indurated so that the mass became light yellow to gray, and as dense and hard as ivory, and it was by this physical change in state, which could be varied within limits by the press that I modified the material from a brisant rupturing explosive to a slow burning propellent.

This is the powder which I styled indurite, and which has been popularly known as the Naval Smokeless Powder.

I was satisfied that I was justified in starting on this new practice in powder-making when I found, on examination of the samples of foreign military powders[1] which later began to reach me officially, that they were heterogeneous mixtures as the old gunpowder is and that they contained matter which was volatile at ordinary temperatures, and when I learned that the nitroglycerin powders cracked from freezing.

I was still more satisfied when I learned the results of the proving tests which were all made except the chemical stability and breaking down tests by naval officers detailed for this purpose at the Proving Ground and elsewhere, and who had no prejudice in its favor. All of the numerous publications which have appeared about it have issued from headquarters, and I present the matter myself here for the first time.

I have appended the data from these trials to this address where, on inspection it will be seen, that after development, the powder in use, in successive rounds, gave remarkably regular pressures and uniform velocities. I was informed by the Chief of the Bureau before the firing trials, recorded in the tables began, that if I could produce a powder giving 2,000 feet initial velocity and but fifteen tons pressure, it would be a complete success. Inspection of the tables show that this was more than realized and that in two successive rounds in the

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[1] Table I.

six-inch rapid fire gun, using twenty-six pounds of my powder and a 100 pound projectile, the pressures were 13.96 and 13.93 tons, and the velocities 2,469 and 2,456 feet per second respectively, while according to the Report of the Secretary of the Navy, 1892, page 26, "the powder manufactured for use in the six-inch rapid fire guns was stored at Indian Head proving ground, through a period of six months, covering a hot summer, and at the end of the time showed no change in a firing test."

On page 25 Secretary Tracy says, "It became apparent to the department early in this administration that unless it was content to fall behind the standard of military and naval progress abroad in respect to powder, it must take some steps to develop and to provide for the manufacture in this country of the new smokeless powder, from which extraordinary results had been obtained in Europe. With this object negotiations were at first attempted looking to the acquisition of the secret of its composition and manufacture. Finding itself unable to accomplish this, the Department turned its attention to the development of a similar product from independent investigation. The history of these investigations and of the successful work performed in this direction at the torpedo station has been recited in previous reports. It is a gratifying fact to be able to show that what we could not obtain through the assistance of others, we succeeded in accomplishing ourselves, and that the results are considerably in advance of those hitherto attained in foreign countries."

From this survey we see that all of the smokeless powders that have met with acceptance and proved of value as ballistic agents with the exception of Indurite are mixtures of one or more of the cellulose nitrates, or mixtures of these bodies, with nitroglycerin or some other oxidizing agent, like barium nitrate, and a restrainer or with a nitro substitution compound and that all have been condensed or hardened into a rubber-like or celluloid-like form, by which, even under the high pressures which obtain in the gun, they are expected to undergo combustion only and that at a moderate and regular rate.

In thus condensing the material, and in determining the best form of grain, it will be observed that we have been guided by the experience gained in the compression of gunpowder, and we have been able to effect this as we have by the experience gained in the development of celluloid, and we have been able to manipulate our product and shape it into grains only by adopting the methods and machines developed in the manufacture of food, while we have been able to test our product and check our results and thus ensure a more rapid and certain advance by the constant use of the pressure gauge and velocimeter. In my opinion, if these resources had not been at command and available the smokeless powder industry would not yet exist.

From what has been said it may properly be inferred that we seek in these new powders all the virtues of the old gunpowder with the addition that the new powder shall be smokeless, impart higher velocities while producing no greater pressures and that less of it shall be required to do the work. These requirements may be summed up as follows:

The conditions that a smokeless powder suitable for a propellent should fulfill are:

1. That it shall be physically and chemically uniform in composition.
2. That it shall be stable and permanent under the varying conditions of temperature and humidity incident to service storage and use for all time.
3. That it shall be sufficiently rigid to resist deformation in transportation and handling.
4. That it shall produce a higher or as high a velocity with as low a pressure as the service charge of black powder for a given piece.
5. That it shall be incapable of undergoing a detonating explosion.
6. That the products of its combustion shall be nearly if not quite gaseous so that there shall be no residue from it and little or no smoke.
7. That it shall produce no noxious or irrespirable gases or vapors.
8. That it shall not unduly erode the piece by developing an excessive temperature.
9. That it shall be as safe as gunpowder in handling and loading.
10. That it shall be no more than ordinarily dangerous to manufacture.

Most of these requirements have been satisfied in several of the powders, but time alone can determine the question of absolute stability and especially as the comparison is instituted with gunpowder which has been under observation for over 500 years.

We can and do apply tests whose results give us some confidence as I did when I exposed Indurite wrapped in felt in an iron vessel to a temperature of 208° F. for six hours without its undergoing change, and again at a temperature of 212° F. for twenty hours before any change was observed, and again to 5° F. without its being affected.

In fact from the outset I have advised the application of most rigid tests and drew up the following scheme for the Navy Department in July, 1891, by which to test Indurite.

"The most important requisite of powder, after passing the proof test, is that it shall retain its characteristics under all the conditions of storage or transportation which may obtain in the service or that, if any change does take place, it shall not cause the powder to develop under the "proof" conditions any greater pressure than it did at the time of proving, and that such falling off in velocity as may result from this change in the powder shall not be relatively greater than that which obtains for service black powder, and shall be uniform for the same conditions of exposure.

"In providing for this test I would first prove a ten pound lot to determine the maximum weight that will come within the limits fixed for pressure and velocity, and then I would load 1000 Winchester 30.1 cal. and 1000 Mannlicher shell with a charge some grains (say five) less than the maximum, so as to be doubly safe in case the pressure should become increased through the treatment to which the powder is subjected.

"The loading should be done with extreme care by skilled workmen in an especially clean and uniformly heated and dried room. The charges should be weighed on chemical balances and with all the precautions surrounding an analytical operation. The balls should be weighed and gauged, and the shell should be gauged so as to secure as nearly absolute uniformity as possible, while the caps and priming (if used) and wads should be identical for each shell of each 1000 lot.

"These being prepared, I would pack these ball cartridges precisely as if ready for issue to the service, and then I would store 385 Winchester's and 385 Mannlicher's in the regular magazine at the Naval Torpedo Station, and the same number of the same kind in the regular magazine at the Naval Ordnance Proving Ground. I would then draw from the magazine at the Torpedo Station twenty-five Winchester's and 25 Maunlicher's and fire them, using the muskets and measuring instruments which are to be used throughout the trials, and I would repeat this trial every month for three years, firing ten rounds of each form of ammunition and using the same muskets and instruments throughout. At the same time I would have an identical set of tests made at the Proving Ground, the same precautions being taken there regarding the instruments and tools. Throughout the tests a close watch should be kept on the magazines by means of maximum and minimum thermometers so that if abnormal results are obtained in firing it may be known whether or not any abnormal conditions have obtained in the magazine. This series of tests will consume 1540 rounds. It would, in my judgment, be of much value to store with these cartridges and fire with them an equal number of charges of standard service black powder, to be used as a standard for reference by which any error in the observations, or defects in the instruments may be detected.

"I would take eighty rounds of the Winchester's and eighty of the Mannlicher's and place them in an oven heated to 140° F. or thereabouts. At the end of one month twenty of each are to be drawn out and this to be repeated each month for four months. One half of each form should be proved at the Torpedo Station and the other half at the Proving Ground.

"I would take eighty rounds of the Winchester's and eighty of the Mannlicher's and subject them for two weeks to the freezing temperature, then for two weeks to a temperature of about 140° F., and then draw twenty of each, and this should be continued until the last forty drawn out have been exposed for eight weeks to freezing and eight weeks to the high temperature. The firing trials with these should be made as with preceding ones.

"The remaining shell should be stored in the regular magazine to be used in any test case which may arise or in any manner suggested by the results obtained in the tests described above.

"In the meantime tests could be made with the hand cut S. P. for the capacity of the powder to resist crumbling and dusting during transportation and the tendency of the fixed ammunition to explode *en masse* by the impact of projectiles, or by the explosion of a single cartridge in the midst of a box filled with them. The first can be effected by taking a pound or a kilogram of carefully sifted powder, placing in a copper vessel which it only partly fills, and attaching it to a shaft so that it will be continually and violently shaken, and allowing this to go on every working day for a week. The powder can then be sifted, using the same mesh as before, the weight of the dust found and the percentage of dusting for the given circumstances determined.

"In the trials for tendency to explode *en masse* fifty or forty-five caliber ammunition can be used and the weights of charges need not be very precise, but the ammunition should be packed in, as nearly as possible, the same way as would obtain in service practice."

We have seen that the development of smokeless powder has been rendered necessary by the improvement in the gun. It now appears that in consequence of the possession of the powder we must further improve the gun for we cannot in our present guns utilize all the energy now available. Experiments looking to this have been going on in France, where in a Canet ten cm. gun of eighty calibers, with a charge of 12.35 pounds of powder and a projectile weighing 28.66 pounds there was obtained the extraordinary muzzle velocity of 3366 feet per second, while the maximum pressure was 18.91 tons per square inch. Longridge, an English authority, deprecates the lengthening of the gun as it becomes too unwieldy and he advocates utilizing the energy of the gun by strengthening it so it will endure greater pressures and then using larger charges. He points out that if this Canet gun were reduced to forty-five calibers, and strengthened, we could obtain from it the same enormous muzzle velocity by increasing the charge to thirteen and a half pounds, though the pressure would rise to twenty-five tons per square inch.

What the result will be where authorities of standing disagree is impossible to foresee, but the fact is demonstrated that the powder is now more highly developed than the gun, and that while seeking for smokelessness, we have secured a propellent which is capable of producing much higher velocities than gunpowder, with all the additional advantages of flat trajectory, increased danger area, greater accuracy, and greater range which follow as consequences.

TABLE I.

COMPOSITION OF VARIOUS POWDERS.

Mark.	Nitro-Cotton.	Guncotton.	Barium Nitrate.	Potassium Nitrate.	Sodium Carbonate.	Volatile.	Cellulose.	Sodium Picrate.	Charcoal.	Humus.	Nitro-Glycerin.	Graphite.
B. N., Aug. 22, '90	26.84	44.42	18.25	3.08	4.92	2.05	....	....	....	....	....	....
B. N., Dec. 5, '90	29.79	40.54	19.00	5.81	3.87	1.50	....	....	....	....	. ..	....
B. N., June 3, '91	38.05	35.55	18.94	1.81	4.51	1.06	....	....	....	....	....	....
B. N., Aug. 12, '91	41.31	29.13	19.00	7.97	2.03	1.43	....	...	....	....	....	....
B. N., Oct. 16, '91	31.38	49.89	17.92	3.43	2.82	0.82	....	....	....	....	....	....
B. N_A., July 9, '90	31.27	40.52	18.42	6.62	2.58	1.25	....	....	....	....	....	....
B. N_C., Aug. 22, '90	32.62	39.44	18.90	7.45	1.39	1.63	....	....	....	....	....	....
B. N_C., Dec. 5, '90	32.03	39.52	19.36	5.17	3.75	0.92	....	....	....	....	....	....
B. N_I., Oct. 16, '91	72.09	26.49	....	....	....	0.92	0.47	trace	....	....	....	....
French Powder, June 3, '91	73.11	25.98	....	. .	....	0.89	....	trace	....	....	....	....
Poudre B., Oct. 16, '91	32.86	66.00	....	....	....	1.14	trace	....	....	....	....	....
Walsrode, S. P., Sept. 4, '90	12.08	86.28	....	....	0.93	0.72	....	....	....	....	....	....
[1]Wetterin, S. P., March 18, '91	46.70	30.35	....	....	....	9.66	....	....	12.39	0.90	....	....
[2]Wetterin, S. P., March 18, '91	48.15	30.73	....	....	....	8.22	....	....	12.12	0.77	....	....
[3]Wetterin, S. P., March 18, '91	47.78	25.87	....	....	....	14.69	...	....	10.84	0.80	....	....
Lebel, Sept. 27, '90	28.21	69.45	....	....	0.80	1.49	....	....	....	....	....	....
German, Oct. 15, '90	10.00	88.43	....	....	0.56	0.99	trace	....	....	....	....	....
Cordite, Sept. 17, '90	7.04	29.20	....	....	[4]6.17	1.30	0.23	....	....	....	56.04	....
Cordite, Oct. 11, '90	8.45	27.72	....	....	[4]4.23	1.45		....	....	....	58.13	....
Ballistite, Sept. 19, '90	44.58	....	....	....	2.44	....	....	....	....	....	52.99	....
Nobel's, S. P., Oct. 15, '90	53.26	0.97	....	....	3.42	0.41	....	....	....	....	41.95	....
Schwab, Nov. 7, '90	77.41	20.42	....	....	0.69	1.47	....	....	...	...	....	trace

[1] Small arm. [2] Small cube. [3] Large cube. [4] Includes dextrine.

Mark.	Nitro-Cotton.	Guncotton.	Barium Nitrate.	Potassium Nitrate.	Sodium Carbonate.	Volatile.	Cellulose.	Sodium Picrate.	Charcoal.	Humus.	Nitro-Glycerin.	Graphite.
[1] Reg. Y., 283, Nov. 14, 90	56.46	....	....	....	0.37	0.33	....	....	....	....	42.84	trace
[2] Reg. Y., 283, Nov. 14, '90	52.10	....	....	...	0.36	0.39	....	....	....	....	47.17	....
German, S. P., Aug. 7, '91	48.83	7.45	....	....	....	0.53	....	....	....	....	43.15	trace
Maxim, flat, June 3, '92	8.14	71.19	....	....	2.58	0.19	....	....	....	....	[3]17.90	....
Maxim, cord, June 3, '92	6.84	46.60	....	....	1.70	0.26	....	....	....	....	[3]44.60	....
Rifleite, May 7, '92	22.48	74.16	....	....	....	0.84	....	....	Manchester yellow 2.52	....	....	trace
S. K., May 6, '92	20.39	57.73	18.08	1.24	....	1.43	....	....	Aurine 1.11	....	....	....
S. R., May 7, '92	28.18	46.97	19.97	2.35	....	1.45	....	....	1.06	....	....	....
E. C., Nov. 9, '91	[4]lignin 53.57	[5]lignin 1.86	34.26	1.48	$NaNO_3$ 3.07	1.17	[6]lignin 3.12	....	Aurine 0.55	....	....	....
Schultze, Sept. 24, '91	27.71	32.66	27.62	2.47	2.88	1.48	1.63	....	Paraffin 4.20	....	....	....
Brackett, Sept. 26, '91	31.43	13.70	....	....	19.76	2.93	13.22	....	....	18.94	....	....
American Wood Pd., Jan. 27, '91	24.90	30.07	....	....	9.76	5.83	19.55	....	....	9.89	....	....
" Grade C., Aug. 27, '91	29.25	14.06	....	....	15.27	3.01	28.08	....	....	10.32	....	....
" " E., Aug. 27, '91	24.91	25.62	....	....	17.81	3.86	19.15	....	....	8.65	....	....
" 10-Bore Trap, Aug. 29, '91	33.21	18.69	....	....	14.82	2.36	20.27	....	....	10.65	....	....
" 12-Bore Trap, Aug. 31, '91	29.47	21.85	....	....	13.38	3.14	16.59	....	....	15.62	....	....
Reine Powder, Dec. 8, '90	....	....	48.44	....	sodium picrate 46.31	1.18	....	....	Charcoal 4.07	....	....	....

[1] Five mm. [2] One mm. [3] Includes castor oil. [4] Soluble nitro-lignin. [5] Insoluble nitro-lignin. [6] Unconverted lignin.

TABLE II.

TESTS OF INDURITE AT NAVAL ORDNANCE PROVING GROUND.

Powder.	*Gun.*	*Weight of Charge.*		*Projectile.* *System.*	*Projectile.* *Weight.*	*Pressure. Tons.*	*Velocity. Foot—seconds.*
Service Black.	Hotchkiss 1 Pdr.	140 grams		Housing	465 grams	11.2	1694
"	"	150 "	Small ignition disk in each charge.	"	450 "	11.2	1690
"	"	150 "		Common shell	450 "	....	1793
"	"	150 "		"	450 "	....	1841
S. P. No. 151, No. 3 T.	"	50 "		"	450 "	....	1341
"	"	70 "		"	450 "	....	1811
"	"	80 "		"	450 "	....	2150
"	"	80 "		Housing	460 "	13.0	1877
"	"	80 "		"	460 "	15.0	1896
"	"	75 "		Common shell	450 "	....	1816
"	"	75 "		"	450 "	....	1760
"	"	75 "		"	450 "	....	1894
S. P. No. 153, No. 4 T.	"	70 "		Housing	465 "	14.2	1774
"	"	70 "		"	465 "	14.4	1616
"	"	70 "		Common shell	450 "	About 12.13 tons	1774
"	"	70 "		"	450 "	"	1776
S. P. No. 157, No. $4\frac{3}{16}$ T.	"	70 "		Housing	465 "	8.2	1082
"	"	90 "		"	465 "	11.2	1363
M. N. 2.	"	100 "	Ignition charge 8 grains. N. X. 9 (Blk. fine grain). Ignited at rear.	"	....	13.5	Lost—missed wires
"	"	90 "		Common shell	Not obs.	Not obs.	1584
"	"	90 "		"	....	9.0	1281
S. P. No. 140.	Hotchkiss 3 Pdr.	100 "		"	3 pounds	1.5	882
"	"	200 "		"	3 "	4.3	Lost
"	"	300 "		"	3 "	15.0	2186
"	"	300 "		"	3 "	12.2	Lost
"	"	300 "		"	3 "	12.0	Lost
"	"	300 "		"	3 "	12.3	2105
"	"	310 "		"	3 "	14.9	2216
"	"	310 "		"	3 "	14.8	2250
S. P. No. 148.	"	275 "		"	....	....	....
"	"	300 "		"	....	9.0	1766

TESTS OF INDURITE AT NAVAL ORDNANCE PROVING GROUND.

Powder.	*Gun.*	*Weight of Charge.*			*Projectile.* *System.*	*Projectile.* *Weight.*	*Pressure.* *Tons.*	*Velocity.* *Foot—seconds.*
S. P. No. 148.	Hotchkiss 3 Pdr.	315	"	Small ignition disc. Priming 89. N. X. Q.	Common shell	....	10.4	1921
"	"	325	"		"	....	11.2	2017
"	"	335	"		"	....	12.2	2076
"	"	338	"		"	....	11.0	1995
"	"	345	'		"	....	15.4	2187
"	"	340	"		"	....	14.3	2166
"	"	340	"		"	....	11.5	2126
"	"	343	"		"	....	18.0	2214
S. P. No. 153, No. 4 T.	"	250	"		"	3.3 lbs.	11.3	1887
"	"	275	"		"	3.3 "	13.6	2051
"	"	300	"		"	3.3 "	24.0	2281
"	"	275	"		"	3.3 "	16.8	1975
"	"	270	"	"	"	3.3 "	14.5	2000
"	"	270	"	"	"	3.3 "	16.0	2018
"	"	270	"	"	"	3.3 "	22.5	2050
S. P. No. 141 a.	Hotchkiss 6 Pdr.	200	"		"	6 "	7.2	1085
"	"	250	"		"	6 "	9.0	1237
"	"	300	"	Ignition charge 8 grams N. X. L. Blk. fine grain.	"	6 "	9.2	1453
"	"	300	"		"	6 "	9.2	1453
"	"	325	"		"	6 "	9.6	1584
"	"	350	"		"	6 "	9.6	1648
"	"	375	"		"	6 "	13.6	1813
"	"	375	"		"	6 "	10.6	1738
"	"	400	"		"	6 "	16.0	1903
"	"	390	"		"	6 "	14.3	1841
"	"	392	"		"	6 "	14.3	1855
S. P. No. 153, No. 4 T.	"	200	"		"	6 "	6.5	1330
"	"	250	"		"	6 "	8.6	1544
"	"	300	"		"	6 "	9.9	1679
"	"	350	"		"	6 "	16.7	1728
"	"	340	"		"	6 "	15.0	Lost

TESTS OF INDURITE AT NAVAL ORDNANCE PROVING GROUND.

				Projectile.			
Powder.	*Gun.*	*Weight of Charge.*		*System.*	*Weight.*	*Pressure. Tons.*	*Velocity. Foot—seconds.*
S. P. No. 153, No. 4 T.	Hotchkiss 6 Pdr.	340 "		Common shell	6 lbs.	18.0	Lost
S. P. No. 157, No. 4$\frac{3}{16}$ T.	"	300 "		"	6 "	5.0	1324
"	"	350 "		"	6 "	6.5	1473
"	"	400 "		"	6 "	11.4	1775
"	"	420 "	Priming 8 grams N. X. L.	"	6 "	9.1	1738
S. P. No. 148, No. 4.	"	300 "		"	6 "	7.6	1543
"	"	350 "		"	6 "	11.1	1751
"	"	365 "		"	6 "	12.0	1818
"	"	372 "		"	6 "	12.5	1835
"	"	382 "		"	6 "	11.0	1862
"	"	392 "		"	6 "	13.0	1920
"	"	410 "		"	6 "	13.6	2002
"	"	418 "		"	6 "	15.0	2047
"	"	418 "		"	6 "	15.0	2047
S. P. No. 148, No. 4.	"	418 "		"	6 "	14.8	2043
"	"	418 "		"	6 "	14.0	2012
"	"	418 "		"	6 "	13.0	1992
M. N. 2.	"	400 "		"	6 "	9.5	1724
"	"	480 "	Priming charge 25 grams of fine grained powder in each charge.	"	6 "	11.6	1988
"	"	480 "		"	6 "	12.0	1992
"	"	440 "		"	6 "	8.0	1702
"	"	450 "		"	6 "	8.0	1728
"	"	450 "		"	6 "	8.1	1735
S. P. No. 146 b.	4-in. No. 11.	4.5 pounds		"	33 "	13.5	1762
S. P. No. 146 a T.	"	4.5 "		"	33 "	10.9	1820
S. P. No. 149 T.	"	2.25 "		"	33 "	3.5	1177
"	"	4.50 "		"	33 "	10.3	1845
"	"	4.75 "		"	33 "	11.5	1945
"	"	5.00 "		"	33 "	13.6	2046
"	"	5.15 "		"	33 "	14.0	2080
"	"	5.25 "		"	33 "	14.2	2083

TESTS OF INDURITE AT NAVAL ORDNANCE PROVING GROUND.

Powder.	*Gun.*	*Weight of Charge.*		*Projectile.* *System.*	*Projectile.* *Weight.*	*Pressure. Tons.*	*Velocity. Foot—seconds.*
S. P. No. 149.	4-in. No. 11.	5.00 "		Common shell	33 lbs.	13.6	Lost
"	"	5.35 "		"	33 "	15.2	Lost
"	"	5.30 "		"	33 "	15.0	1943
"	"	5.30 "	Ignited at rear.	"	33 "	15.0	2122
S. P. No. 159 M.	"	3.5 "		"	33 "	9.5	Lost
"	"	4.05 "		"	33 "	10.3	1912
"	"	4.2 "		"	33 "	11.0	1936
"	"	4.8 "		"	33 "	12.0	1990
"	"	5.2 "		"	33 "	14.7	2125
"	"	5.2 "		"	33 "	14.8	2134
"	"	5.3 "		"	33 "	14.8	2145
S. P. No. 149 M.	"	5.3 "		"	33 "	15.0	2160
"	"	5.3 "		"	33 "	14.8	2158
S. P. M. N. 2 (163).	"	4 "		"	33 "	7.5	1591
"	"	5 "	One ignition grain in base of each charge. Ignition at rear.	"	33 "	10.2	1888
"	"	5.5 "		"	33 "	12.35	1993
"	"	5.5 "		"	33 "	12.35	1997
"	"	4 "		"	33 "	7.3	1606
"	"	4 "		"	33 "	7.2	1569
"	"	5 "		"	33 "	10.5	1892
"	"	5 "		"	33 "	10.2	1865
S. P. No. 159 M. N. 2.	6-in. No. 120.	9.5 "		"	77 "	6.5	1728
"	"	13⅛ "		"	77 "	10.0	2131
"	"	15 "		"	77 "	11.9	2281
"	"	16¼ "		"	77 "	13.6	2415
S. P. M. N. 3, No. 162.	"	11½ "		"	100 "	5.0	1466
"	"	15 "		"	100 "	7.9	1784
"	"	18 "		"	100 "	11.0	2060
"	"	20 "		"	100 "	13.2	2212
"	"	21 "		"	100 "	14.4	2312
" After 6 mos.	"	14 "		"	100 "	6.7	1678
" storage.	"	20 "		"	100 "	12.0	2170

TESTS OF INDURITE AT NAVAL ORDNANCE PROVING GROUND.

Powder.	*Gun.*	*Weight of Charge.*	*Projectile.* *System.*	*Projectile.* *Weight.*	*Pressure. Tons.*	*Velocity. Foot—seconds.*
S. P. M. N. 6.	6-in. No. 120.	15 "	Common shell	100 lbs.	5.06	1535
"	"	19 "	"	100 "	7.30	1793
"	"	23 "	"	100 "	11.20	2151
"	"	25 "	"	100 "	12.56	2369
"	"	26 "	"	100 "	13.96	2469
"	"	26 "	"	100 "	13.93	2456
S. P. M. N. 3, No. 162.	"	7 "	"	50 "	4	1496
"	"	11 "	"	50 "	10	2108
"	5-in. "	7 "	"	50 "	4	1496
"		11 "	"	50 "	10	2108
"		12 "	"	50 "	12	2256
"		12.75 "	"	50 "	13.2	2383
"		13.12 "	"	50 "	14.2	2474
"		13.4 "	"	50 "	15.6	2578
S. P. M. N. 2 (168).	4-in. R. F. No. 8.	5¼ "	"	33 "	12.4	1997
"	"	5½ "	"	33 "	13.4	2042

ACIDITY OF MILK INCREASED BY BORACIC ACID.

By E. H. Farrington.

Received July 22, 1896.

WHILE making some investigations with milk preservatives, the writer noticed that sweet milk in which a small quantity of boracic acid (preservaline) was dissolved, required what appeared to be an abnormally large quantity of one-tenth normal alkali to neutralize it and much more than water in which the same amount of "preservaline" was dissolved. One-half gram of preservaline was dissolved in 500 cc. water, and twenty cc. of this solution required one cc. of one-tenth normal alkali to produce the pink color, when phenolphthalein was used as an indicator in titrating. Before adding preservaline the water had a neutral reaction.

One-half gram preservaline was dissolved in 500 cc. of sweet milk, and twenty cc. of it required eight cc. of one-tenth normal alkali to give the pink color, although before adding the preservaline twenty cc. of this same milk gave the pink color with only four cc. of one-tenth normal alkali.

The same amount of preservaline increased the acidity of a given quantity of milk four times as much as it did the acidity of the water.

The writer is unable to explain this reaction, but it gives a simple means of detecting preservaline or boracic acid in milk, as normal milk will smell or taste sour when it contains as much natural acidity as is represented by eight cc. of one-tenth normal alkali to twenty cc. milk. This represents 0.36 per cent. lactic acid, and it can be safely stated that milk which contains over three-tenths per cent. lactic acid and neither tastes or smells sour, has been adulterated with some preservative, probably boracic acid.

Dairy School,
University of Wisconsin.

CORRESPONDENCE.

UNITED STATES DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
WASHINGTON, D. C., JULY 23, 1896.

Editor Journal of the American Chemical Society, Easton, Pa.:

DEAR SIR:—A majority of the Executive Committee has decided to call the annual meeting of the Association of Official Agricultural Chemists for Nov. 6, 7 and 9, 1896. These dates immediately precede the meetings of the Association of Agricultural Colleges and Experiment Stations, which will convene in Washington, Nov. 10. The session will be held, as heretofore, in the lecture hall of the National Museum, at Washington, D. C.

The Ebbitt House offers to the Association entertainment at the rate of $3.00 per day and the free use of its parlors for committee meetings, if desired. The Ebbitt House is on the corner of "F" and 14th Sts., and can be reached from all stations by the "F" St. or Avenue cars.

Respectfully,
H. W. WILEY,
Secretary A. O. A. C.

BOOKS RECEIVED.

Bulletin No. 42. Second Series. Horticulture. Louisiana State Experiment Station, Baton Rouge, La. 1896. 44 pp.

Bulletin No. 123. Examination of Food Products sold in Connecticut. Connecticut Agricultural Experiment Station, New Haven, Conn. July, 1896. 79 pp.

Transactions of the American Institute of Mining Engineers. Vol. xxv. February to October, 1895, inclusive. New York City: Published by the Institute. 1896. xvii, 1068 pp.

Part III. Geology and Agriculture. A preliminary report upon the Florida parishes of East Louisiana and the Bluff. Prairie and Hill Lands of Southwest Louisiana. By W. W. Clendenin, A.M., M.S., Geologist. Louisiana Experiment Station, Baton Rouge, La. 96 pp.

ERRATA.

On page 667, August number, 12th line from bottom, in equation, for *o.3b* read *o.3y*.

On page 668, 2nd line from top, for *Dividing* read *Multiplying*.

VOL. XVIII. [OCTOBER, 1896.] NO. 10.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.

BY W. W. ANDREWS.

Received August 7, 1896.

IN the years 1883 and 1884 two papers were published by Dr. Eugene Haanel, of Victoria College, Cobourg, Ontario, now of Syracuse University, in the Proceedings of the Royal Society of Canada, in which he described the brilliant results he was able to obtain in the production of the Bunsen iodide films on the blowpipe support then proposed for the first time; namely, thin tablets of plaster of Paris made by casting sheets three-sixteenths of an inch thick on panes of glass and scratching them, before hardening, with ruled lines, so that when set they would readily break into oblongs measuring two and one-half by one and one-quarter inches. The pure white and highly polished surface of these tablets and its great power of condensing heated gases and exhibiting the true colors, their cheapness, thermal and hygroscopic properties of the tablets, the ease with which they may be prepared and carried, and the excellence of the results when the sublimed iodides, bromides, oxides and sulphides are deposited as coatings upon them, make them an ideal form of support in blowpipe work.

A small pit is made at one end of the tablet somewhat larger than a pin's head, and in this the ore to be tested is heated. The oxide coatings are produced by heating the substance *per se*, the bromides by adding to the substance a drop of fuming hydrobromic acid, and the iodides by adding a strong solution of hydriodic acid (made by dissolving five ounces of metallic iodine in seven ounces of water, by passing a steady stream of hydrogen sulphide through the solution while the iodine is slowly added). All who have experimented with this solution will be ready to admit that it yields superb results, but though easily renewable when one is near a hydrogen sulphide generator it is very unstable, takes a long time to prepare and is troublesome to carry.

In 1890 Mr. F. A. Bowman read a paper before the Nova Scotia Natural History Society, in which was described a search for a solid reagent to replace the hydrogen iodide solution. He found that potassium hydrogen sulphide or any alkaline sulphate, which does not yield a coating of its own, mixed with potassium iodide would do very well. He also found that microcosmic salt and potassium iodide gave good results. This mixture is a favorite one with some blowpipe experts. Tin is the only metal in the three series of the periodic table, beginning with copper, silver and gold, which does not yield a characteristic coating with this reagent.

The writer has not been able to find whether there have been any other reagents besides these seriously proposed. Plaster of Paris as a support is mentioned in Moses and Parsons' late work as an alternative to charcoal. This is, as far as known to the writer, the only standard work, in which the colors of the films on the tablets are described.

In the rapid development of other methods in chemical work the blowpipe has fallen largely into disuse, and for many years, besides the work outlined above and that of Col. Ross and some valuable tests for individual elements proposed by Chapman, little or no advance has been made. There are two possible lines of future progress in blowpiping, one in the direction of increased power and simplicity, so as to make the method more valuable for the field work of the mineralogist, geologist and prospector, and the other in the direction of increased range and delicacy until the dry way tests rival the delicacy and distinctiveness of the wet tests, as they surpass them in expeditiousness. It may not be amiss, therefore, to call attention to the instrument of Plattner and Berzelius, which, in its modern form as the hot-blast blowpipe and with the new support and the new reagents and reactions now known to chemistry, is an instrument surpassed by the electric furnace only.

The cleanliness of the method here described, as compared with the charcoal method and the quickness with which sure results can be obtained with very small amounts, should call the blowpipe back to the table of the chemist for preliminary and confirmatory tests, to class work as an accompaniment of the wet methods, and to the lecture table for the purposes of illustration. It is possible to detect five or six metals in presence of each other on one tablet. Many of the coatings are permanent and are all renewable on reheating with addition of a drop of the reagent, so that a set of tablets carefully labelled with a pencil forms a permanent record of a set of experiments. The value of this to the practical chemist and to the student need not be emphasized. It may be noted that blowpiping is so much of an art that new methods are seldom well enough practiced, by those who have become skillful in other methods, to reveal their value.

The extensions of the plaster of Paris method here proposed are: A set of new reagents, which yield some new reactions which are of value in detecting elements in the presence of each other, notably gold and copper in very small amounts in the presence of all elements so far experimented with; arsenic, tin and antimony in presence of each other; sulphur in the presence of selenium and tellurium, and chlorine, bromine and iodine in the presence of each other; a new set of film tests which are found to be of great delicacy (the limits of delicacy are now being measured, it being found that gold, one part in one million, and copper, one part in four millions, are easily detectable); a change in the composition of the tablets which does away with the necessity for using platinum wire in the production of the colored glasses with borax and metaphosphoric acid, these being formed on the tablets with a decided gain in facility and delicacy; and lastly several new methods of handling the tablets themselves.

It is evident that solid reagents will always be the more convenient to carry afield, but, in the laboratory, liquids are to be preferred, since they are more readily applied, and when the assay is heated, the reagent, which has soaked into the tablet, is fed steadily toward the hot portion of the tablet, so that the heated assay is constantly enveloped in the vapor of the reagent. For over two years the writer has used with satisfaction the following reagents, which have been selected from a score of experimental ones. They are stable and almost odorless, can be carried to the field in a solid form and so used if need be, while a few seconds suffice to prepare them in liquid form if it be desired so to use them.

The chief reagent is a saturated solution of iodine in a strong solution of potassium thiocyanate in water. The solution takes place almost instantly and with great absorption of heat. The bottleful now in use has been in use for over two years, a little of one or other of the ingredients being added from time to time as seemed to be required. Exact proportions are not necessary to the efficiency of the reagent. It can be prepared on the field from the solid chemicals at a moment's notice. The brilliancy of the iodide films produced with this solution are not one whit behind those possible with the pure solution of hydriodic acid. Its coatings tend to form in definite bands of color. The spheres of desposition of the iodide and the oxy-iodide are sometimes very well defined. Some striking and important variations are produced by the presence of the potassium thiocyanate, for example, with molybdenum, osmium, iridium, tin, antimony, lead, bismuth, cadmium and mercury.

Dr. Haanel showed in his second paper that by means of hydrobromic acid, copper and iron could be detected at one operation in the presence of each other and in the presence of nickel and cobalt and any other flux-coloring substances. Instead of the fuming acid with its dangerous properties, a mixture in molecular proportions of powdered potassium bromide and metaphosphoric acid, or potassium hydrogen phosphate or sulphate may be used. This, suggested by Bowman's work, suggests further a set of solid reagents, made by using potassium chloride, potassium fluoride and potassium iodide with metaphosphoric acid, and these form a valuable set for special tests. They have the advantage of yielding at once the colored flux and the coatings produced by any volatile matter in the assay.

When heated, the reaction represented by the following general equation takes place: $KX + HPO_3 = KPO_3 + HX$.

These two reagents, the iodine solution and the bromide mixture, suffice for the production of coatings. The following which are used to differentiate them, are dropped upon the oxide or iodide film and colored spots are produced, or the color is discharged to white (technically, *wiped*), or the coating disappears through solution and absorption by the tablet.

Dr. Haanel used ammonium hydroxide and yellow ammonium sulphide for the purpose of testing the solubility of the films and to produce the sulphide spots. Both of these are troublesome to carry, and the latter is objectionable on account of its intolerable odor, its instability and the fact that for its renewal the hydrogen sulphide generator is required. It has been found that a solution of potassium sulphide, strong enough to show a clear amber color, made by dissolving the solid potassium sulphide in water, or by boiling a strong solution of potassium hydroxide with an excess of flowers of sulphur till the solution assumes a blackish color, which on cooling will be amber yellow, fulfils all the required conditions. If through the action of light it is decomposed, all that is necessary for its renewal is to boil the solution and perhaps add a little sulphur. We therefore have a reagent which can be carried as a solid, can be renewed anywhere, is as efficient as the ammonium sulphide solution and is almost odorless.

In the place of ammonium hydroxide a solution of potassium cyanide is used, made a little more stable by the addition of a little ammonium or potassium hydroxide. Besides these the common acids of the laboratory are useful and a solution of potassium thiocyanate.

The potassium thiocyanate solution is used in two ways. It is either dropped on the coating to test its solubility and to note the colors produced after heating, or it is dropped on the tablet before the coating is deposited, and then the hot vapors sweeping over the moist spot, give with some metals characteristic reactions.

Those coatings which are pure white and therefore invisible on the white tablet, are examined on a tablet which has been smoked in a flame, or on one streaked up the middle by means of a glass rod which has been dipped in a solution of boric and metaphosphoric acids mixed with lampblack or bone charcoal. In this way the coatings may be viewed on a white and on a black surface at the same time.

In order that the colored fluxes may be made on the tablets, the latter must be made more resistant to the dissolving effect of the metaphosphoric acid and the alkali in the borax. If one teaspoonful of boric acid be added to each quart of the water used in making the tablets, they will be found to be denser and to have the necessary quality. Borax can be fused on them without gathering any impurities from the plaster and if metaphosphoric acid be substituted for phosphor salt, we have a flux which will spread upon the tablet and exhibit the colors of all degrees of saturation at the same time. This reagent, first proposed by Ross, who described its reactions, is preferable to microcosmic salt, since, as it contains no volatile matter and melts readily to a clear glass, it will show by effervescence the presence of water or carbon dioxide, or other gas in a mineral. With cobalt it yields a fine violet when cold, which becomes blue on the addition of any of the alkali metals, for which therefore it furnishes a ready test. The only objection to this reagent is the tendency of the sticks to deliquesce, but a piece can be kept in a corked test-tube,[1] which can be readily dried over the flame, if dampness should gather. In dry weather it causes no trouble. Its solvent power is very great and the colors are fine. Ross asserts that silica and zirconia are the only oxides which are not soluble in this flux. The whole operation may be completed in the time usually required to form the bead in the platinum wire loop and the volatile oxide films will be found on the tablet above the glass, where they may be tested with potassium sulphide and the other reagents. One operation, therefore, suffices for the determination of the volatile acid elements, the volatile metal or metals, and flux-coloring metal. Metaphosphoric acid well replaces potassium hydrogen sulphate in the operation as

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[1] In this laboratory each student is supplied with a set of very small dipping tubes and a wooden block into which holes are bored for the reception of a set of test-tubes closed with paraffined corks, to hold the reagents.

described in most text-books for the detection of carbon monoxide, carbon dioxide, iron, chlorine, bromine, iodine, nitrogen tetroxide, chlorine tetroxide, sulphur dioxide, hydrogen sulphide, hydrocyanic acid and acetic acid.

DESCRIPTIVE LIST OF REACTIONS OBTAINABLE ON THE TABLETS.

Copper *per se* yields with difficulty a coating of volatilized metal. With the iodine solution it yields a white iodide coating and an emerald green flame. The iodide treated with a drop of potassium sulphide gives with gentle heat a blackish gray, which is removed by greater heat. Potassium cyanide and nitric acid dissolve the sulphide; hydrochloric and sulphuric acids have no effect till heated and then they remove the spot. Potassium thiocyanate applied to the coating has no effect till heated, when a gray spot is shown. Any part of the coating touched with the tip of the flame shows the emerald green flame (Haanel). Metaphosphoric acid glass is greenish-blue when hot and a fine robin's egg blue when cold. Metaphosphoric acid and potassium bromide yield a splendid reddish violet coating of copper bromide (compare osmium). The bromide plus potassium sulphide shows a brown, which if heated turns blackish and then green, not affected by sulphuric acid, but immediately destroyed by a drop of nitric acid.

Copper plus metaphosphoric acid and potassium chloride yields a yellow brown cupric chloride, which, if treated with a drop of potassium thiocyanate, gives a black ring, which, if heated, becomes a black spot. If, before the assay is heated, a drop of nitric acid be placed one-half inch from the assay and a drop of potassium thiocyanate be placed above that, on heating a fine and very volatile blue-black coating is deposited far up the tablet. This blue-black is not affected by acetic acid, is wiped off by sulphuric acid slowly, and immediately by hydrochloric and nitric acid. The formula of this compound will be determined if some method be found, by which it may be collected in quantity. (See chlorine.)

Silver gives *per se* a pinkish gray coating, which touched by the blowpipe flame (flamed) becomes mottled brown. Reduced globules are often shown. Metaphosphoric acid yields the same coating and a pearl-like glass. The iodine solution yields a pale yellow, paler when cold, and around the assay forms a black, which does not fuse into the tablet (compare lead). Flaming with oxidizing flame yields a mottled brown anywhere on the tablet. This is a very delicate test and as all other coatings are volatile, the flame drives them off and leaves the silver oxide. Potassium sulphide produces a spotted blackish brown, probably potassium silver sulphide, the analogue of ammonium silver oxide, for if treated with a drop of potassium cyanide it immediately disappears, but if it be first heated, the potassium cyanide has no effect. If only one-half of the sulphide spot be touched with the tip of the flame and then the potassium cyanide be applied, the untouched portion will disappear while the other half will remain. Potassium thiocyanate on the iodide wipes it off; when heated the spot turns black, which is not wiped off by potassium cyanide.

Gold is slightly volatile *per se* and more so if a solution of iodine in potassium iodide be used as a reagent, and the result is a fine rose-colored film of the metal. If potassium thiocyanate be present, no volatility is noticed. Gold and the other elements which respond to the new tests will be the subject of another paper.

Zinc *per se* yields a white coating, not very volatile and luminous yellow when hot. Potassium sulphide and potassium thiocyanate produce no visible change on zinc films. The iodide film is a white, which treated in any part with cobalt nitrate solution yields the well-known zincate of cobalt, which is quickly decomposed by a drop of nitric acid (compare tin). This reaction obtained in this way is decisive for zinc, as aluminum and silicon do not volatilize and are therefore not present in the coating. In the metaphosphoric acid glass, zinc causes flashes of light and detonations (Chapman). Metallic zinc sometimes yields *per se* a black sublimate along with the white oxide (compare arsenic.)

Cadmium *per se* yields one of the most beautiful of the oxide films, which consists of a rich brown with black farther away and somewhat iridescent near the assay. Acetic acid does not affect it; potassium cyanide dissolves it at once (compare cadmium sulphide). Potassium sulphide and potassium thiocyanate yield a scarlet when hot, and bright yellow, cold. This cadmium sulphide is not affected by potassium cyanide, is quickly destroyed by nitric acid, less readily by hydrochloric acid, immediately by acetic acid (compare cadmium oxide), and is not affected by sulphuric acid (compare copper).

The iodide coating is white with well-defined borders, which is easily distinguished in the presence of other white coatings by the *per se* and sulphide reactions. In the assay and near it the sulphide reaction will be seen caused by the potassium thiocyanate in the iodine solution (see sulphur). In metaphosphoric acid cadmium acts like zinc and yields at the same time its oxide coating beyond the glass.

Mercury gives *per se* a very volatile film of mercury snow, which, with a feather, may be swept into a globule. It is not affected by the other reagents.

The iodide coating is a splendid combination of scarlet, yellow, and velvety green. This is caused by the mixing of the green mercurous iodide with the scarlet and yellow forms of the mercuric iodide. The reactions of each kind of iodide may be obtained on the one tablet. The green and the scarlet are the stable forms into which the coating changes on standing. A drop of the reagent or some more of the vapor blown across the coating changes all into the scarlet form. With mercurous iodide, sulphuric acid gives a yellow spot (mercurous sulphate). Potassium hydroxide gives a black; so does ammonium hydroxide, (iodomercurosamine, NH_2Hg_2I), and potassium sulphide. With the mercuric iodide, sulphuric acid increases the amount of the scarlet, potassium hydroxide yields a white, as does ammonium hydroxide (iodomercurosamine) and potassium sulphide, yield a white spot, quickly turning black. The sulphide spot, strange to say, is partially dissolved in nitric and hydrochloric acid, while sulphuric acid turns it brownish. Potassium cyanide yields a black and potassium thiocyanate a dark spot, and if heated both are wholly volatilized (compare lead, bismuth, and silver). Water has no effect on this coating (compare lead), nor have hydrochloric, nitric, or sulphuric acids. By the last the coating is not readily wetted.

Gallium has not been experimented with. Indium yields a pale yellow iodide coating and a blue flame.

Thallium *per se* yields a feathery brown with white farther away and a green flame (compare arsenic and tellurium). Potassium sulphide gives a terra cotta brown spot with a black ring. Potassium cyanide and potassium thiocyanate have no effect upon it. The iodide film is an egg yellow with a purple black veil farther away. Potassium sulphide gives a rich brown which potassium cyanide darkens. Hydrochloric acid discharges it slowly and yellow is left (compare bismuth and tellurium). Potassium thiocyanate has no effect on the yellow or the black till heated, when it yields a white (compare bismuth, tellurium, tin, and lead). Potassium cyanide dissolves the black but has no effect on the yellow. Sulphuric acid has no effect. A drop of the reagent on the coating heated shows a spreading black and an orange ring.

Carbon yields a sooty coating, which comes better if sulphuric acid or metaphosphoric acid be used upon the assay. In the case of the carbonates, boric oxide or metaphosphoric acid yield an odorless effervescence (Ross, Chapman). Organic acids blacken the tablet when heated.

Silicon. An interesting reaction given by the silicates, especially the hydrous forms, is being investigated. Chapman dissolves a silicate in boric oxide and then precipitates the silica by adding metaphosphoric acid.

Germanium will give a light yellow iodide film, but none has been on hand to experiment with.

Tin gives a slightly volatile coating, showing a trace of brown when hot. Potassium thiocyanate, if dropped on the oxide and strongly heated gives a pale yellowish green, infusible (compare lead). The slight volatility of tin oxide suggests a scale of volatility, of great use in describing the formation of the films on the tablets. The scale runs in the order of increasing volatility: tin, zinc, cadmium, and mercury. Anything less volatile than tin might be classed as non-volatile.

The iodine solution yields a yellow, reddish brown when hot, the brown fading instantly. Potassium sulphide yields a black with a brown edge, which darkens on heating. Potassium cyanide discharges the color, which turns black on heating, and when strongly heated shows the pale yellowish green (stannous thiocyanate, $Sn(SCN)_2$; compare lead, bismuth, arsenic, mercury and zinc). Water decomposes the film with formation of oxy-iodide.

Cobalt nitrate gives the bluish green, which is not so readily attacked by nitric acid as the zinc green.

Antimony tri- or pentachloride yields with all tin salts a fine purplish blue-black coating, stable in the presence of acids. Potassium thiocyanate decomposes it when heated and forms the pale green.

These tests with iodine, antimony trichloride, and with potassium thiocyanate remove tin from the list of metals determinable with difficulty before the blowpipe. They can be depended on through a wide range of mixtures.

Lead yields *per se* a white and yellow; reddish brown when hot. All lead salts fuse into the tablet with the formation of lead plumbate, one of the constituents of glass. Potassium sulphide produces a brownish black, with reddish brown ring.

The iodine solution gives a film which is chrome yellow, with a band of fainter yellow farther away (oxy-iodide?), and the assay is black. Potassium sulphide yields a spot with the reddish brown edge. Hydrochloric acid destroys the edge at once. Nitric acid wipes the spot off slowly, and sulphuric acid destroys the black and restores the yellow. The very volatile paler yellow on the outer edges is turned to a brighter color by the same treatment (compare mercury). Potassium cyanide produces a slight paleing of the sulphide color. Potassium thiocyanate on the iodide film gives a black ring, which heated becomes a black spot (compare bismuth). Water wipes off the coating (compare mercury, arsenic and silver).

The bromide film made by using potassium bromide and potassium hydrogen sulphate presents some interesting differences. It is white with a trace of yellow, the yellow fusing into the tablet. Potassium sulphide gives a spot, greenish for a moment and then black, on which potassium cyanide and potassium thiocyanate have no effect, but is partly destroyed by hydrochloric acid, more rapidly by nitric acid, and completely by sulphuric acid. Potassium thiocyanate, placed on the sulphide and heated, gives a black ring; with greater heat, a yellow, and still greater heat, a greenish gray ring. Potassium cyanide on the iodide film has no effect till heated; then a white. Potassium thiocyanate has no effect on iodide till heated; then a yellowish spot appears (compare tin). The sulphide heated becomes grayish black, on which nitric acid and the other acids have no effect (compare copper).

It is a good illustration of Carnelley's law of color that in general the bromide film of any metal resembles the iodide film of an element either in a higher series in its own family or in the same series, in another family toward the left in the natural classification. Thus the bismuth bromide film resembles the iodide film of antimony and lead. Lead bromide resembles tin and thallium iodide. Thallium resembles mercury, and mercury resembles silver in the same way.

Nitrogen with metaphosphoric acid in the nitrates yields an effervescence with the fumes, odor and reactions of nitrogen tetroxide farther up the tablet, and in the cyanides, the odor of hydrocyanic acid. Nitrates with carbonaceous matter yield ammonia, which will cause white fumes to rise from a spot on the tablet moistened with hydrochloric acid. Ross reports that any nitrogen compound with boric oxide yields a tough transparent bead, and with metaphosphoric acid, purple in the reducing flame with manganese dioxide.

Vanadium gives with metaphosphoric acid a pale yellow in the oxidizing flame, and in the reducing flame a green. (Ross).

Phosphorus. A great desideratum in blowpipe analysis is a good test for this element and the phosphates.

Arsenic yields *per se* a brownish black with a white film falling farther away with odor of garlic and blue flame (compare thallium and tellurium). The iodide coat is white and pale yellow; the assay wholly volatile. Potassium sulphide, with a drop of hydrochloric acid, forms the yellow sulphide, little affected by acids. If oxalic acid be applied to a sulphide spot and then hydrochloric acid, no effect is noticeable. The yellow will show up still better next day (compare antimony). If a drop of potassium thiocyanate be placed on the tablet about one inch above the assay, and between them a drop of nitric acid and the arsenical vapor be blown over them from the assay, there will generally be formed in the edge of the potassium thiocyanate spot a bright bluish green of unknown composition. All common acids except acetic destroy it. It shows well in the presence of salts of tin and antimony. When it does appear it is decisive for arsenic. This iodide film exhibits a very marked repulsive power for water, probably due to the arsenic oxide which forms with it. Potassium iodide with metaphosphoric acid yields more of the yellow than does the iodine solution.

Antimony *per se* yields a white and yellow band and white fumes. Potassium sulphide yields on this an orange brown, which is quickly destroyed by a drop of nitric acid.

The iodide film is a fine orange yellow far away with yellow nearer the assay and abundant white fumes. Potassium sulphide yields, especially when heated, an orange red with a rich brown and then a black beyond the spot. Hydrochloric acid slightly heated destroys it; nitric acid destroys it instantly; so also does its vapor. Potassium thiocyanate wipes the coating, but heated it yields a fine brown, which is permanent when exposed for months. Potassium cyanide wipes the coat. The orange yellow sulphide spot, produced on the iodide film obtained with potassium iodide and metaphosphoric acid, is not so susceptible to the action of nitric acid and is more rapidly destroyed by hydrochloric acid than the one described above.

If arsenic be present with antimony, there will be shown inside the yellowish orange of the iodide film, a fine peachy pink, which is hard to wet. Stannic chloride yields with antimony in most combinations a purplish blue-black, which is remarkably stable (Haanel). It is now being collected in quantity, with a view to the determination of its formula. It will be seen that with the blue with potassium thiocyanate, the rose pink, and the reactions of the sulphide with hydrochloric, nitric and oxalic acids, the presence of arsenic can be easily demonstrated in the presence of antimony and, as far as experiment has gone, in the presence of any other substances.

Bismuth yields *per se* a yellow ring near the assay and often a brittle globule. Potassium sulphide gives on the white oxide a brownish black which nitric acid destroys and on which hydrochloric acid has little effect till heated, when it removes it completely. Sulphuric acid has no effect. Potassium thiocyanate on the oxide produces a yellow ring, and heated a yellow spot turning black. (It is to be noted that potassium thiocyanate itself when heated or treated with strong acids, shows on the tablet a fine yellow, which further heating renders colorless.)

The iodide film is a splendid combination of chocolate black, crimson and yellow, the assay turning black. Potassium sulphide forms a chocolate black, soluble in nitric acid and not effected by sulphuric acid. The latter acid on the iodide film produces a black and a dull red edge. This is probably the sulphide formed by the reduction of the acid by the decomposition products of the potassium thiocyanate, which fall with the iodides. It has been noticed, however, to happen with no other metal than bismuth. This reaction is very useful in detecting small quantities of bismuth in the presence of other metals giving dark colored films (compare tellurium). Potassium thiocyanate on the iodide wipes it off, forming a yellow ring, but when heated it forms a black spot with a brown ring. Potassium cyanide also wipes the iodide, but when heated forms a dark gray spot. Glacial acetic acid wipes off the yellow and the crimson, but has no effect on the chocolate iodide.

Sulphur. In looking for a better test for sulphur than the ordinary one with soda and a piece of silver, the stability at high temperatures and the two brilliant and characteristic colors of cadmium sulphide attracted attention, and the fact that it is easily formed in the presence of potassium cyanide. To a solution of cadmium bromide, potassium cyanide was added till precipitation took place and then the solution of the precipitate as potassium cadmium cyanide. This, dropped on a fragment of the sulphide and heated, will show on the tablet near the assay a brilliant scarlet when hot, and bright yellow when cold. This is not affected by potassium cyanide (compare cadmium oxide). One great advantage of this is that selenium and tellurium do not yield anything which can be confounded with these colors, selenium giving a grayish brown and tellurium a yellowish brown. Sulphates may be reduced by potassium cyanide, or by glycerol. A sulphide or sulphate fused with potassium cyanide will, if touched with a drop of ferric chloride, show in the tablet the pinkish red of ferric thiocyanate. The sulphur in the tablet causes no trouble.

Selenium and tellurium are further differentiated from sulphur by their characteristic films, which are tests of great delicacy. Twenty-seven varieties of complex sulphides, such as bournonite, tetrahedrite, stannite, etc., and all of the common sulphides and sulphates, were found to respond to this test at once.

Selenium yields *per se* with characteristic odor and flame a fine reddish brown, almost pure red on the outer edges and black on the inner edges near the assay. Potassium cyanide wipes it off, while potassium thiocyanate has no effect, except that, if it be heated, a very stable red compound is formed (KSeCN ?).

The iodide film forms in color very similar to the *per se* coat, but more volatile. Potassium sulphide yields a yellow. Potassium cyanide wipes the iodide film off instantly, and therefore will reveal the presence of any other element not so affected, whose film might be hidden by the pronounced hues of the selenium film. Potassium thiocyanate has no effect, while it and heat wipe off most other coatings, and therefore will reveal the presence of selenium in obscuring associations, such as lead. Sulphuric acid shows a slight tendency to make this coating darker (compare bismuth).

Tellurium gives *per se* with flame and odor a brownish black with a white film falling nearer the assay (compare arsenic). Sulphuric acid, if gently heated, shows an effervescent pink of tellurium sulphate. Acetic acid wipes off this coat (compare cadmium). So do the potassium cyanide and ammonia fumes. The iodide film is brownish and purplish black, less brown than the *per se* coat. Potassium cyanide wipes it off in the cold. Potassium thiocyanate has no effect on the purple (compare thallium), and slightly dissolves the brown, and if nitric acid be added a yellow appears. Potassium sulphide darkens the coating a little. Sulphuric acid acts as on *per se* film.

Chromium yields an assay which is dark green when hot and a fine green on cooling. This test can be made very delicate. Metaphosphoric acid gives similar colors.

Molybdenum yields *per se*, and especially by flaming, an ultramarine coating. The oxide film, which forms when the iodine solution is used, comes better by flaming of the film and in presence of vapors of sulphuric acid. A potassium thiocyanate spot, over which the vapors from the assay have swept, exhibits a splendid hyacinthine pink. Metaphosphoric and sulphuric acid vapors aid its formation. It is probably molybdenum thiocyanate ($Mo(SCN)_2$). If potassium thiocyanate be added to the assay this color will spread all around the edges of the blue, extending to a distance of two inches from the assay. This very delicate reaction is of special interest, from the fact that it shows that part of the potassium thiocyanate, or at least the radical thiocyanogen travels undecomposed that distance over the tablet and that all these films are formed in the presence of moist potassium thiocyanate or thiocyanogen vapors, which will account for the behavior of some of the films. This pink is decolorized by ammonia, not restored by nitric acid. Sulphuric acid dropped on the tablet will form a blue ring ($MoSO_4$). Metaphosphoric acid yields blue or bluish green glasses according to the degree of saturation (Ross).

Tungsten and uranium in metaphosphoric in the reducing flame yield, the former a blue and the latter a green glass (Ross).

Fluorine. If a fluoride be mixed with phosphoric acid and a piece of glass be laid on the tablet about two cm. away from the assay, a fine etched semicircle will show itself after the heating of the assay. The radius of the semicircle is about three cm. long.

Manganese yields with metaphosphoric acid a glass, which is violet hot and cold, colorless in the reducing flame, and turning green on the addition of an excess of soda (Chapman, Ross).

Chlorine. Chlorides, bromides and iodides of the alkali metals yield *per se* white coatings, which may be distinguished from other white coatings by their flames and by the action of a small quantity of the coating scraped together and mixed with the metaphosphoric acid cobalt glass, which will remain blue on cooling.

A compound of chlorine if mixed with metaphosphoric acid and heated, in the reducing flame (if oxy salt), will cause white fumes to rise from a spot moistened with ammonia situated about two cm. above the assay. If a copper salt be present in the glass or near it, so that copper chloride vapors are formed and these are allowed to sweep over a spot of nitric acid and then over one of potassium thiocyanate, near the assay a yellowish brown coating of cupric chloride will form with an azure blue flame, and beyond the potassium thiocyanate spot a fine blue-black, very volatile (see copper).

A bromide with potassium cyanide added to it and the fused mass laid upon a copper glass and a drop of nitric acid added, a fine red will show itself. Bromides with metaphosphoric acid saturated with copper, upon blowing, yield a fine and very volatile reddish violet coating. If a bismuth salt be exposed to the hot vapors, it will yield a yellow coating. The spot on the tablet moistened with starch paste, not too near the assay, will turn yellow.

Similarly treated iodine compounds yield violet vapors, a violet in the glass appearing with effervescence, and with copper salt they yield a white coating, with bismuth scarlet and chocolate, and with starch a bluish black.

Iron gives an iodide film too delicate in color to show up well, either on the white or the black surface. Its presence can be shown by a red coloration after blowing hydrochloric acid vapors over the tablet, to turn all ferrous compounds into ferric, and then adding a drop of potassium thiocyanate to the coating. It is difficult to obtain plaster of Paris sufficiently pure not to give this reaction for iron. Such reaction can, however, be readily distinguished from that given by an assay. Metaphosphoric acid gives a luminous yellow when hot, which is perfectly colorless when cold. A drop of acid on this to produce ferric compounds, followed by a drop of potassium thiocyanate, will show the red of ferric thiocyanate, which is decolorized by phosphoric acid, but not by hydrochloric acid. Made in this way this test is not too delicate to show the iron of composition. An assay of iron treated with a drop of sulphuric acid and heated will show on the tablet a film of Venetian red.

Cobalt yields a glass blue hot, and violet cold; permanently blue if alkali be present. Boron trioxide acts similarly. With the iodine solution a spot around the assay turns pink, then deep blue on heating, and then black.

Nickel with boron trioxide separates as green fragments, which may be gathered by solution of the glass in water, and then the separated nickel (as any nickel compound) will yield in metaphosphoric acid, a reddish brown when hot and amber yellow when cold (Ross).

Palladium gives a dull blue-black film with the iodine solution, which is very characteristic. The assay turns dull black.

Osmium yields *per se* a greenish black. The iodide film is a combination of olive green, dove and slate colors, with red appearing around the lower edges. The edge of the coating nearest the assay shows greenish brown and the assay itself will be closely surrounded with an iridescent black film. Potassium sulphide turns the coating somewhat darker, which heated, becomes a brownish film, which is wiped off by hydrochloric and nitric acids and not affected by sulphuric acid and potassium cyanide. On the iodide films sulphuric acid has no effect; potassium thiocyanate has none till heated and then it turns brown. Hydrochloric and nitric acids remove the film. Potassium thiocyanate dropped on the tablet over an inch from the assay before the coating is deposited, will, when the vapors sweep over it, turn to a fine brick red, destroyed by potassium cyanide and the acids.

Potassium bromide and potassium hydrogen sulphate give a pinkish brown (compare copper). Potassium sulphide produces a gray not affected, which turns darker on being heated, destroyed by acids, and not affected by potassium cyanide.

Iridium yields with the iodide solution an indistinct brownish yellow coating and a potassium thiocyanate spot which in tint resembles the molybdenum spot, but it is covered with dots of darker pink.

Platinum gives an infusible gray film. Ruthenium and rhodium are being investigated.

All these reactions have been obtained from a large number of the compounds of each element except in the cases of osmium, indium and iridium. The writer will be glad to hear of any cases in which they fail and to receive specimens of combinations which cannot be unlocked by this method. One gram weight of any alloy is sufficient. The next work to be undertaken is to exhaustively determine the lowest percentage of any metal which can be determined with certainty in the presence of one, two, or any number of other metals, to describe the characteristic effect that one metal has on the coating yielded by another when they are deposited together and to determine the value of each metal as an interfering element.

COVERED TABLETS.

The tablets are easily cut with a knife and therefore they can be used in various ways. Open tube work can be performed on a tablet, if a groove be cut lengthwise of a tablet and laid upon another, groove down. A small pit for the assay is cut in the lower one about one centimeter from the end. The groove is cut so that its narrowest part is just above the assay pit, and from that point to the lower end it flares into a half funnel form and into this the flame is blown. By regulating the size of the groove at its narrowest part the amount of air which will flow over the assay may be regulated. This method is of great use when very small quantities of precipitates are to be tested. For instance, five-tenths mg. of arsenious oxide gave in one experiment a narrow coating one-half inch long on each tablet. This gives ample opportunity for making confirmatory tests. Various reagents may be placed along the groove to be acted on by the vapors, gold leaf for mercury, potassium cadmium cyanide and lead acetate for hydrogen sulphide fumes, starch, bismuth and antimony solutions for iodine, copper sulphate for chlorine, etc.

If a coating be made, or a small piece of volatile salt be placed in a small pit in the tablet and a thin tablet be placed over it, it is found that if potassium sulphide, or potassium thiocyanate be dropped on the upper tablet and the flame be directed upon the drop, they will pass through the tablet and reactions will take place away from the air. After a few seconds blowing the upper tablet will be found to be floating on a layer of hot gas, which flows between the two smooth surfaces. Tin and arsenic, and other substances easily oxidizing in the air, form their sulphides very readily under these conditions. Potassium thiocyanate forms sulphides. It is in this way possible, by using ammonium hydroxide or hydrochloric acid, to form the sulphides in the presence of moist acid or alkaline vapors.

Other methods of using the tablets will be described later.

In teaching research methods, the plaster of Paris method is one of the finest instruments to use with beginners. In the course of an hour a student will have been able to make from twenty to forty different tests and without any delay in preparing solutions, or in waiting for filtration to take place, he will have produced the oxide, sulphide, chloride, bromide, and iodide of a given metal, and will have noted their colors, manner of deposition, volatility, solubility in several reagents, and the behavior of the assay itself at high temperatures and will have ransacked his vocabulary to find terms to describe the phenomena in his written notes. His skill in manipulation and his powers of observation are kept in liveliest exercise and his independence developed, for it is quite possible to give each student in a large class his own problem. In no other laboratory work do the compelled acts of judgment follow each other as rapidly. There are many problems which may be set requiring reference to standard chemical literature, and many simple and some very difficult equations of reactions to be written.

Not the least valuable consideration from an educational standpoint, is the aesthetic quality of the work. All the coatings are symmetrical in form and beautiful in shading, and many of them in brilliancy of hue and in delicacy of shading, rival the most splendid colors of flowers. This gives added interest to the work and is of great value since adult students are so frequently found to be greatly deficient in the color-sense, as children are not. There has not been opportunity to compare the shades of these films with the descriptions given in the Standard Dictionary. When this has been done, exact training can be given in color language also.

Apology is offered for publishing the results of this research at this stage, when so many unsolved problems stand along its path, but this much is given in order that the practical value of these reactions and methods may be put to the test.

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AN ANALYTICAL INVESTIGATION OF THE HYDROLYSIS OF STARCH BY ACIDS.

BY GEO. W. ROLFE AND GEO. DEFREN.

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FEW problems of commercial analysis have been so complicated and so discouraging as that of the determination of the components of starch conversion products. The well-known schemes of commercial analysis of worts and similar products of the action of diastase are based on the assumption that but two simple compounds are formed from the starch—maltose and dextrin. In the case of glucose syrups and starch sugars, which are the results of acid hydrolysis, it is known that the reaction proceeds farther as dextrose is formed from the maltose and dextrin.

Musculus and Gruber[1] decided that these reactions went on together so that except at the very beginning or final stage of hydrolysis all of these compounds must be present in solution.

The analysis of acid-converted starch products must therefore take into consideration the presence of the third compound, dextrose.

Much doubt, however, has been thrown on the accuracy of such analyses, as during the past twenty years the researches of O'Sullivan, Brown, Heron, Morris, Bondonneau, Herzfeld, Musculus, Bruckner, Fischer, and other distinguished investigators, have shown that not only the simple compounds referred to can be isolated from starch products but also many others of quite distinct optical and chemical properties. Space will not permit a review of this work, which is in many points conflicting. The recent conclusion of Lintner and Düll is that the following compounds result from hydrolysis :[2]

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[1] *Bull. Soc. Chim.*, 2, 30.

[2] *Ber. d. chem. Ges.*, 28, 1522–1531.

Hydrolysis with oxalic acid.	With diastase.
Amylodextrin	Amylodextrin
Erythrodextrin I	Erythrodextrin I
" IIα	......
" IIβ	......
Achroodextrin I	Achroodextrin I
" II	" II
Isomaltose	Isomaltose
Dextrose	Maltose

Others, as Brown and Morris,[1] deny the existence of the isomaltose of Fischer and Lintner and Düll, and mention another compound, maltodextrin, an intermediate between dextrin and maltose.

In 1885 Brown and Morris[2] discovered the remarkable law that at any stage of the conversion of starch by diastase, the total product, in its optical properties and relation to Fehling solution, behaved exactly as if made up of two components only, maltose and dextrin, so that it was possible by taking the rotatory power to calculate at once the cupric reducing power if the total carbohydrates were known. This law indicated that, however complicated the bodies isolated, they could be considered as existing in solution as two simple compounds, and did much to establish the validity of the principles of the usual commercial analyses of beer-worts and similar products.

The method of analysis of glucose syrups and starch sugars implies the assumption of a similar law, but the proof that this law actually exists under varying conditions of hydrolysis apparently has not been worked out.[3]

Our investigations have been made, first, to determine whether there was any simple constant relation between the optical rotation and the cupric reducing powers of starch products hydrolyzed under different conditions; and, secondly, whether any laws could be found affecting the three simple bodies assumed to be formed and determined by the usual methods of analysis.

Incidentally we have collected some data as to the speed of hydrolysis, influence of carbohydrates on specific gravity of

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[1] *J. Chem. Soc.*, No. 393. Aug., 1895.

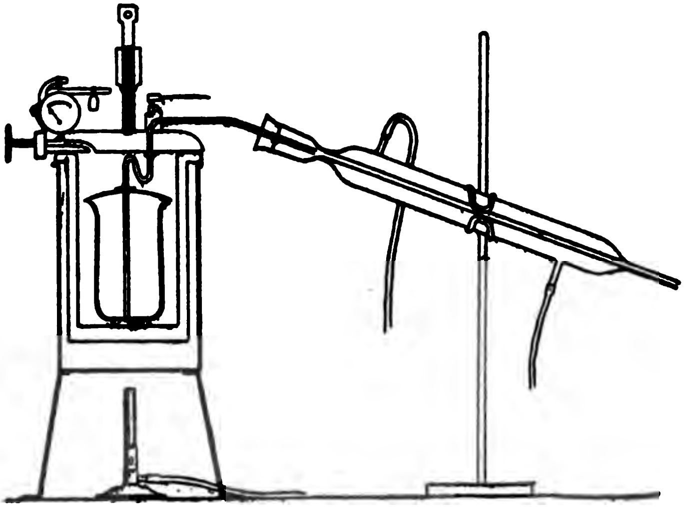
[2] *Ann. Chem.* (Liebig), 231, 131.

[3] A very complete bibliography of the original publications on the carbohydrates is in *Tollen's Handbuch der Kohlenhydrate*, Vol. 1, *1888*, 331-360; Vol. II, *1895*, 368-398.

solutions, and some looking to the adoption of a more rapid and accurate method of determining cupric reducing power by Fehling solution.

The latter data are included in a separate paper. The work on specific gravities is not yet sufficiently complete for publication.

An autoclave of the usual construction was modified in the following manner: The thermometer tube was taken out and in its place was attached a specially constructed valve, by means of which liquor cooking in a beaker in the interior could be removed at any time during the progress of the experiment. This superheated liquor was prevented from vaporizing by passing through a condenser. Excessive condensation into the beaker was prevented in large part by a well fitting lead cap. The illustration sufficiently explains the apparatus.



In most of the work about 100 grams of a good quality of commercial corn starch[1] was mixed with a liter of water con-

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[1] An analysis of this starch by the usual commercial methods gave:

	Per cent.
Starch	89.15
Oil	0.14
Ash	0.12
Albuminoid	0.42
Water	10.21
	100.04

taining the hydrolyzing acid. Samples of from fifty to seventy-five cc. of the liquor were removed at different stages of the conversion and immediately shaken up with a few grams of marble dust. Two drops of tenth normal sodium hydroxide solution were then added to the sample, which was cooled and filtered. This method of neutralization, except in cases of very low converted samples, gave an absolutely clear filtrate, the filtration being exceedingly rapid, and the removal of the albuminoids being practically complete. Low-converted products often required to be heated with aluminum hydroxide before filtering.

The samples were tested as follows:

(1) For specific gravity by Westphal Balance, corrected to a temperature of 15.5° C.

(2) Specific rotatory power ($[\alpha]_D$) by a Schmidt and Haensch half-shade saccharimeter.

(3) Cupric reducing power by means of Fehling solution.

Total Solids—Total solids were calculated from the specific gravity of the solution by the factor 0.00386, which was taken to represent the influence of one gram of the mixed carbohydrates in 100 cc. of solution. Corrections were made when necessary for the influence of other substances in solution, not carbohydrates. This factor 386 is practically that of Balling and Brix and has been found exact for approximately ten per cent. solutions of cane sugar, and the balance of evidence seems to be that it is correct for starch products.

We have made several determinations of this factor by drying ten cc. of solution on rolls of dried paper at a temperature of 100–105° C. Our results point to the constancy of this factor 386 even in solutions of low rotatory power, but are not yet complete enough to establish the value for all rotations.

Therefore, in this work we have adopted the expedient used by Brown and Morris, and others, and calculated all optical and copper reduction constants on the assumption that all three carbohydrates in solution affect the specific gravity like cane sugar when the concentration is approximately ten per cent. Even if subsequent investigations show that this view is not exactly correct, the relative values of the constant will not be appreciably affected nor the truth of the laws as set forth.

To illustrate this method of calculation of constants we give the following from our own determinations:

Ten grams of dextrose dissolved in 100 cc. of water gave a rotation of 30.70° on the Schmidt and Haensch saccharimeter. This gives $[\alpha]_D$ as 52.8.[1] As the increase in specific gravity per gram of crystallized dextrose in 100 cc. is 0.00381, $[\alpha]_{D_{386}}$ is 53.5.

9.751 grams of crystallized maltose anhydride in 100 cc. of water gave a rotation of 76.40. This gives an absolute specific rotatory power of 136.6. The specific gravity factor of maltose being 0.00390, $[\alpha]_{D_{386}}$ is 135.2°. No exact figure is known for the influence of crystallized dextrin on the specific gravity of its solution. O'Sullivan gives 0.00385, and the balance of evidence seems to favor this. Hence 195 is probably correct for $[\alpha]_{D_{386}}$.[2]

In like manner the values for *K* have been reduced to a dextrose with the factor 386.

Specific Rotatory Power.—All readings were made as nearly as possible at a temperature of 20° C. in 200 mm. tubes, the mean of several readings being taken. Corrections for zero-error were made frequently, and the instrument was carefully screened by glass plates from the heat of the lamps. Comparisons were made with a Laurent polariscope to determine the value of the division in terms of angular degrees for sodium light, the accuracy of the quartz wedges having being verified previously. With standard quartz plates the usual factor 0.346 was obtained, but solutions of commercial glucose of approximately ten per cent. gave the figure 0.344, which agrees with the recent work of Rimbach[3] and other investigators. We have taken, therefore, the latter factor in our calculation.

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[1] Precautions against bi-rotation were taken in both examples cited.

[2] Brown and Hearn: *Ann. Chem.* (Liebig), 199, 190–243.

[3] *Ber. d. chem. Ges.*, 27, 2282.

TABLE A.

COMPARISON OF SCHMIDT AND HAENSCH HALF-SHADE SACCHARIMETER WITH THAT OF LAURENT POLARISCOPE READING IN ANGULAR DEGREES.

Test.	S. and H. saccharimeter. (Using bat-wing burner and lens.) Reading.	Zero error.	Corrected reading.	Laurent polariscope. (Sodium flame.) Reading.	Zero error.	Corrected reading.	Factor.
(t = 20—22)							
Quartz A	62.965	0.300	62.665	21° 40′	0	21.666°	0.3457
"	62.800	0.150	62.650	21° 40′	0	21.666°	0.3458
"	62.970	0.290	62.680	21° 40.2′	0.6′	21.660°	0.3458
"	62.836	0.130	62.706	21° 40.7′	c.6′	21.666°	0.3455
Glucose A...	77.510	0.277	77.233	26° 35′	0	26.582°	0.3442
" B...	76.355	0.150	76.205	26° 15.3′	0	26.254°	0.3445
" B...	76.355	0.150	76.205	26° 14′	0	26.233°	0.3442
" C...	76.535	0.150	76.385	26° 18′	0	26.300°	0.3443
" D...	76.110	0.130	75.980	26° 10.3′	0.6′	26.162°	0.3443
(t = 25)							
Hydrolized starch products E.	92.73[1]	00	92.73	31° 56′	—1′	31.95°	0.3445
Hydrolized starch products F.	24.84	00	24.84	8° 32′	—1′	8.55°	0.3442

Cupric Reducing Power.—Our method is practically that of O'Sullivan, first published in 1876. The copper is weighed as the oxide. We have found this method exact and rapid. An analytical investigation of this process has been made by one of us and given in detail in a separate paper.

Plotted Results.—To show the relationship of the copper-reducing power, and the specific rotatory power of the products formed during the progress of the hydrolysis of the starch, we have plotted our results, taking as abscissae the decreasing values of the rotatory power, from the amylodextrin stage (195°) to that of dextrose ($[\alpha]_{D_{386}} = 53.5°$), and as ordinates the cupric reducing power (K_{386}) taking that of an equivalent weight of dextrose as 100.[2] [See Plate A.]

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[1] Using Welsbach burner.

[2] Data given in Table B.

TABLE B.

HYDROLYSIS OF STARCH. EXPERIMENTAL DATA.

Run.	No. of sample.	Minutes Cooking.	grams starch.	Atmospheric pressure.	Acid. Kind.	Acid.	Amount cc.	Water cc.	Sp. gr. 15.5.	Sacch. reading.	Copper oxide.	$[\alpha]_D$ 386.	K 386.
8a	2	30	110	2	HCl	$\frac{n}{10}$	10	990	1.0456	98.0	0.1552	142.7	0.4747
	3	45							1.0394	59.3	0.2103	99.95	0.7480
	4	75							1.0374	41.5	0.2275	73.67	0.8537
	5	135							1.0367	32.9	0.2480	59.53	0.9283
10	1	15	110	2	HCl	$\frac{n}{10}$	10	990	1.0199	57.3	0.0060	191.30	0.0412
	2	45							1.0320	84.8	0.0366	176.0	0.1567
	3	75							1.0348	80.7	0.0923	154.0	0.3652
	4	100							1.0315	67.6	0.1026	142.5	0.4523
	5	130							1.0315	60.8	0.1258	128.1	0.5584
	6	160							1.0318	54.6	0.1368	114.0	0.5993
	7	190							1.0318	49.4	0.1594	103.1	0.6995
	8	220							1.0318	44.7	0.1781	93.95	0.7827
	9	250							1.0323	42.2	0.1848	86.66	0.8000
	10	280							1.0323	38.4	0.1940	78.94	0.8407
11	1	15	110	2	HCl	$\frac{n}{10}$	100	900	1.0414	89.55	0.1290	143.6	0.4434
	2	30							1.0417	55.95	0.2320	89.10	0.7825
	3	45							1.0419	41.0	0.2747	64.98	0.9230
	4	60							1.0414	36.0	0.2837	57.75	0.9663
	5	75							1.0412	33.0	0.2830	53.19	0.9685
	6	90							1.0406	32.5	0.2763	53.16	0.9590
13	1	15	110	2	HCl	$\frac{n}{10}$	100	900	1.0394	103.2	0.0056	174.0	0.1958
	2	45							1.0384	75.7	0.1500	129.9	0.5405
	3	60							1.0380	61.1	0.1898	105.7	0.6988
	4	90							1.0380	45.5	0.2339	79.50	0.8646
	5	120							1.0375		0.2448	67.75	0.9175
14	2	22½	110	2	HCl	$\frac{n}{10}$	100	900	1.0379	97.8	0.0661	167.4	0.2415
	3	35							1.0384	85.9	0.1095	148.6	0.3964
	4	52½							1.0370	64.75	0.1664	116.2	0.6279
	5	75							1.0374	50.80	0.2040	90.20	0.7640

HYDROLYSIS OF STARCH. EXPERIMENTAL DATA.

Run.	No. of sample.	Minutes cooking.	grams starch.	Atmospheric pressure.	Acid.				Sp. gr. 15.5.	Sacch. reading	Copper oxide.	$[\alpha]_D$ 386.	K 386.
					Kind.		Amount cc.	Water cc.					
	6	105							1.0374	39.60	0.2281	70.31	0.8561
	7	135							1.0374	34.95	0.2493	62.34	0.9367
15	2	30	110	2	HCl	$\frac{n}{10}$	1000		1.0371	88.1	0.0890	157.7	0.3329
	3	60							1.0337	67.05	0.1247	132.1	0.5146
	4	90							1.0337	56.50	0.1551	111.4	0.6421
	5	120							1.0337	46.00	0.1863	90.65	0.7727
16	1	25	110	2	HCl	$\frac{n}{10}$	1000		1.0327	79.90	0.0679	162.3	0.2877
	2	40							1.0393	81.40	0.1395	137.5	0.4946
	3	50							1.0380	70.60	0.1617	123.4	0.5936
	4	75							1.0380	57.00	0.1994	99.61	0.7348
17	1	15	55	2	HCl	$\frac{n}{10}$	25	475	1.0360	105.5	0.0173	188.5	0.0643
	2	23							1.0341	92.9	0.0344	180.9	0.1393
	3	33							1.0343	88.1	0.0539	170.6	0.2173
	4	42							1.0352	86.2	0.0751	162.7	0.2963
	5	50							1.0308	79.5	0.0828	157.0	0.3396
18	1	75	60	2	HCl	$\frac{n}{10}$	50	450	1.0422	74.7	0.1892	117.6	0.6273
	2	90							1.0423	68.0	0.2100	106.8	0.6958
	3	110							1.0428	60.3	0.2369	93.56	0.7796
	4	120							1.0428	52.6	0.2587	81.62	0.8507
	5	135							1.0429	49.2	0.2676	76.05	0.8720
19	1	15	60	2	HCl	$\frac{n}{10}$	50	450	1.0383	105.0	0.0329	182.1	0.1186
	2	30							1.0374	87.0	0.0975	154.5	0.3619
	3	40							1.0374	66.2	0.1337	117.6	0.6255
	4	130							1.0359	39.8	0.2272	73.62	0.8882
	5	150							1.0326	34.8	0.2093	70.89	0.8997
20	1	45	60	2	$H_2C_2O_4$	$\frac{n}{10}$	50	450	1.0327	87.2	0.0396	177.1	0.1673
	2	90							1.0301	71.2	0.0766	157.7	0.3526
	3	120							1.0318	65.8	0.1125	135.5	0.4917
21	2	60	60	2	$H_2C_2O_4$	$\frac{n}{10}$	100	400	1.0352	75.9	0.1145	143.2	0.4523

HYDROLYSIS OF STARCH. EXPERIMENTAL DATA.

Run.	No. of sample.	Minutes cooking.	grams starch.	Atmospheric pressure.	Acid. Kind.		Amount cc.	Water cc.	Sp. gr. 15.5.	Sacch. reading	Copper oxide.	$[\alpha]_D$ 386.	K_{386}.
	3	75							1.0359	71.6	0.1350	132.4	0.5237
	4	105							1.0355	64.0	0.1577	119.8	0.6200
24	1	30	65	2	HCl	$\frac{n}{10}$	100	400	1.0440	88.2	0.1651	133.1	0.5236
	3	60							1.0371	38.1	2x(0.1211)	68.19	0.9080
	4	75							1.0376	33.95	2x(0.1319)	59.95	0.9745
	5	90							1.0406	34.7	2x(0.1388)	56.75	0.9526
25	1	45	65	2	$H_2C_2O_4$	$\frac{n}{10}$	200	300	1.0414	99.7	0.0966	159.9	0.3240
	2	90							1.0448	85.6	0.1799	126.9	0.5611
	3	135							1.0452	67.0	2x(0.1265)	98.42	0.7791
	4	180							1.0458	55.3	2x(0.1401)	80.17	0.8525
	5	225							1.0455	47.7	2x(0.1483)	69.61	0.9088
26	1	30	65	2	H_2SO_4	$\frac{n}{10}$	100	400	1.0447	110.9	0.0869	164.7	0.2760
	2	62							1.0466	89.3	2x(0.0821)	127.3	0.5480
	3	90							1.0478	74.2	2x(0.1227)	103.[illegible]	0.7144
	4	120							1.0500	63.1	2x(0.1475)	83.79	0.8206
	5	150							1.0525	56.4	2x(0.1614)	70.96	0.8848
27	1	10	60	4	HCl	$\frac{n}{10}$	50	450	1.0430	95.2	0.1281	147.0	0.4144
	2	20							1.0430	60.85	2x(0.1196)	93.97	0.7738
	3	30							1.0430	42.7	2x(0.1414)	65.94	0.9162
	4	45							1.0430	35.3	2x(0.1466)	54.51	0.9506
	5	60							1.0430	34.8	2x(0.1533)	53.70	0.9968
33	1	10	60	4	HCl	$\frac{n}{10}$	100	400	1.0426	60.8	0.2351	94.77	0.7754
	2	15							1.0426	41.4	0.2833	64.54	0.9378
	3	20							1.0423	35.4	0.2919	55.58	0.9736
34	1	10	60	3	HCl	$\frac{n}{10}$	200	300	1.0435	56.4	0.2532	86.10	0.8143
35	1	90	60	1	HCl	$\frac{n}{10}$	100	400	1.0381	87.6	0.0992	152.7	0.3616
	2	180							1.0391	66.5	0.1887	112.9	0.6751
	3	225							1.0403	49.5	0.2525	81.56	0.8831
39	2	90	60	4	HCl	$\frac{n}{10}$	50	450	1.0384	39.7	0.2621	53.01	0.9607
	3	120							1.0378	30.4	0.2628	53.40	0.9779

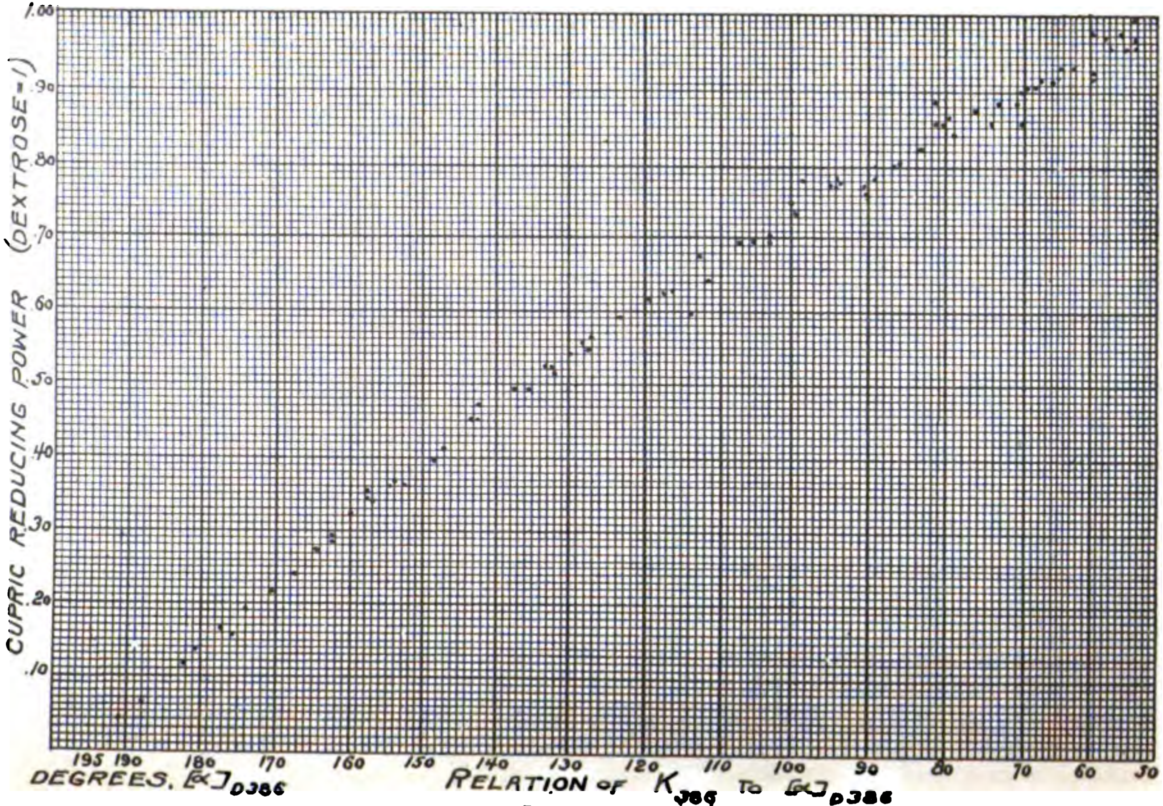
1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
CUPRIC REDUCING POWER (DEXTROSE = 1)
195 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50
DEGREES. $[\alpha]_{D386}$
RELATION OF K_{386} TO $[\alpha]_{D386}$

PLATE A.

The results point to the remarkable fact that the cupric reducing power of the total product bears a constant relation to the specific rotatory power, even when the starch is hydrolyzed under widely varying conditions. Hence, given the one, the value of the other can be calculated. To a rotation of about 90°, the plotted results outline with extraordinary exactness the arc of a circle, the equation of which is

$$x^2 + y^2 + 468x - 646y + 1580 = 0,$$

which exactly intercepts the "zero" and "hundred" points at 195 and 53.5, respectively. The upper part of the curve is not so well defined, the results showing more discrepancy at the high conversion stages. This may be due to some decomposition and the formation of "reversion" products as stated by Wohl,[1] Maercker, Ost, and others. Wohl's figures show the maximum amount of dextrose possible to be 92.7 per cent. of the theoretical quantity. Others give ninety-six to ninety-seven per cent., the missing dextrose being supposed to be converted into dextrin-like bodies identical with those variously described as "gallisin," "isomaltose," etc. We have experimented but little along this line, having made but one hydrolysis with this special object, using $\frac{N}{100}$ hydrochloric acid at four atmospheres pressure, with the following results:

Time of cooking.	$[\alpha]_D$.
60 minutes	55.24
90 "	53.09
120 "	53.40
150 "	54.42

While several of our own results at the low rotations show a cupric reducing power of only about ninety-six per cent. of that of pure dextrose, we do not think that we are justified in arriving at any definite conclusion with the data at hand.

That the solutions begin to color considerably at rotations beyond 90° is, moreover, a strong indication of such decomposition. On the other hand, this accounts for much of the discrepancy of the plot at this part of the curve, as it is exceedingly difficult to get accurate readings on the saccharimeter of these highly colored solutions. Obviously, too, slight errors in the

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[1] *Ber. d. chem. Ges.*, 23, 2101.

readings affect the calculations of the rotatory power the most at these lowest rotations.

Quite as noteworthy are the curves[1] plotted by taking the values of maltose, dextrin, and dextrose as computed for every five degrees of rotation from the values of K, as given by this curve.

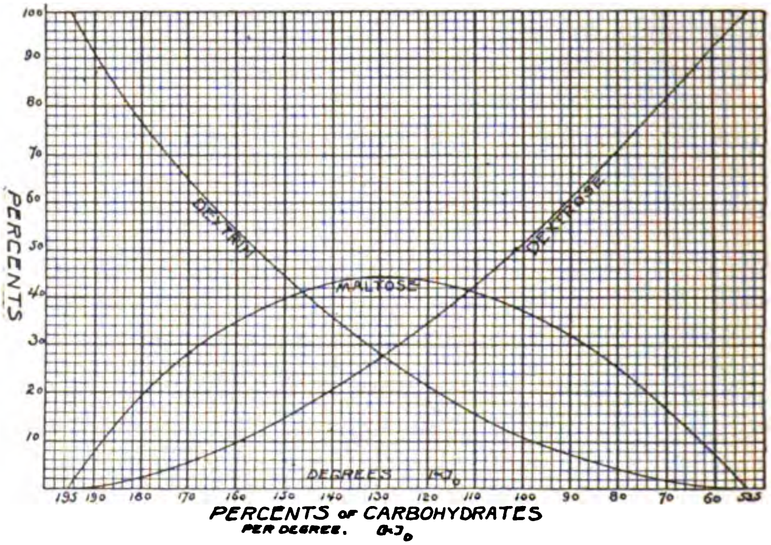

PLATE B.

In this work we have figured constants for solids estimated from the specific gravities of solutions by the factor, 386, and calculated percentages by the well-known equations:

$$g + m + d = 1.00$$
$$g + 0.61m = K$$
$$195d + 135.2m + 53.5g = \alpha$$

Where g is per cent. dextrose,
m is per cent. maltose,
and d is per cent. dextrin.

$$\text{Hence, } m = \frac{d + 141.5K - 195}{27.82}$$

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[1] See plate B.

Examining these curves we see that the dextrin starting from the maximum of 100 per cent. gradually falls to zero near the rotation corresponding to dextrose, while the maltose gradually rises, reaches a maximum percentage of 44.1 at about 129° rotation, corresponding to the usual state of conversion of commercial glucose, and then falls, disappearing at 53.5°. The dextrose, on the contrary, steadily mounts to 100 per cent. It will be noted, too, that at the point of maximum maltose the dextrin and dextrose, as shown by the intersection of the curves, are present in equal quantity.

Tests with phenylhydrazin acetate show the presence of the dextrose distinctly at about 185°, and we had hoped to prove the gradual rise of the dextrose percentage by means of the dextrosazon. While copious precipitates of this beautiful compound were obtained, any attempt of ours to isolate it in anything like quantitative amounts proved a failure, even in solutions containing a known amount of pure dextrose. We hope to take this up more fully in a later investigation.

We have also calculated a table (Table C) from the curves giving the value of maltose, dextrose, and dextrin within one-tenth per cent. for successive stages of acid hydrolysis represented by each degree of rotation between 195 and 53.5. This table, calculated for the factor 386, makes no allowance for possible decomposition of high-converted products.

TABLE C.

CALCULATED VALUES OF CUPRIC REDUCING POWERS AND PARTS OF MALTOSE, DEXTROSE AND DEXTRIN PER UNIT OF CARBOHYDRATE FOR EACH DEGREE OF ROTATION OF A NORMALLY HYDROLYZED STARCH SOLUTION.

$[\alpha]^{20}_{D\,386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
195	0.000	0.000	0.000	1.000
194	0.011	0.017	0.001	0.982
193	0.022	0.033	0.001	0.966
192	0.032	0.048	0.002	0.950
191	0.041	0.063	0.002	0.935
190	0.051	0.079	0.003	0.918
189	0.061	0.094	0.004	0.902
188	0.071	0.110	0.005	0.885
187	0.081	0.123	0.007	0.870

$[\alpha]^{20}_{D\,386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
186	0.090	0.135	0.009	0.856
185	0.100	0.147	0.010	0.843
184	0.109	0.160	0.013	0.827
183	0.118	0.171	0.016	0.813
182	0.127	0.182	0.019	0.799
181	0.137	0.192	0.022	0.786
180	0.146	0.203	0.025	0.772
179	0.155	0.212	0.028	0.760
178	0.164	0.222	0.031	0.747
177	0.173	0.231	0.034	0.735
176	0.182	0.240	0.037	0.723
175	0.191	0.250	0.040	0.710
174	0.199	0.257	0.043	0.700
173	0.207	0.265	0.047	0.688
172	0.216	0.273	0.050	0.677
171	0.224	0.280	0.054	0.666
170	0.233	0.287	0.058	0.655
169	0.242	0.294	0.062	0.644
168	0.251	0.301	0.066	0.633
167	0.259	0.307	0.071	0.622
166	0.267	0.314	0.075	0.611
165	0.275	0.320	0.080	0.600
164	0.283	0.326	0.084	0.590
163	0.292	0.332	0.089	0.579
162	0.300	0.338	0.093	0.569
161	0.308	0.344	0.098	0.558
160	0.316	0.349	0.103	0.548
159	0.324	0.356	0.107	0.537
158	0.332	0.362	0.111	0.527
157	0.340	0.369	0.115	0.516
156	0.348	0.373	0.121	0.506
155	0.356	0.378	0.126	0.496
154	0.365	0.383	0.130	0.487
153	0.373	0.388	0.135	0.477
152	0.381	0.392	0.141	0.467
151	0.389	0.397	0.146	0.457
150	0.397	0.401	0.153	0.446
149	0.404	0.405	0.157	0.438
148	0.412	0.408	0.163	0.429
147	0.419	0.412	0.164	0.420
146	0.427	0.415	0.174	0.411
145	0.435	0.415	0.182	0.403
144	0.442	0.421	0.186	0.393
143	0.450	0.423	0.192	0.385

$[\alpha]^{20}_{D_{386}}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
142	0.458	0.425	0.199	0.376
141	0.465	0.427	0.205	0.368
140	0.473	0.428	0.212	0.360
139	0.481	0.431	0.217	0.352
138	0.488	0.432	0.224	0.344
137	0.496	0.434	0.231	0.335
136	0.503	0.436	0.237	0.327
135	0.510	0.437	0.243	0.320
134	0.517	0.438	0.249	0.313
133	0.524	0.439	0.256	0.305
132	0.531	0.439	0.263	0.298
131	0.538	0.440	0.270	0.290
130	0.546	0.440	0.277	0.283
129	0.553	0.441	0.284	0.275
128	0.560	0.441	0.291	0.268
127	0.567	0.440	0.298	0.262
126	0.574	0.440	0.305	0.255
125	0.580	0.439	0.313	0.248
124	0.588	0.438	0.320	0.242
123	0.595	0.438	0.327	0.235
122	0.602	0.437	0.335	0.228
121	0.608	0.436	0.343	0.221
120	0.614	0.435	0.350	0.215
119	0.621	0.433	0.358	0.209
118	0.628	0.431	0.366	0.203
117	0.635	0.429	0.374	0.197
116	0.642	0.428	0.381	0.191
115	0.649	0.425	0.390	0.185
114	0.656	0.422	0.398	0.180
113	0.663	0.420	0.408	0.174
112	0.669	0.417	0.414	0.169
111	0.675	0.414	0.423	0.164
110	0.681	0.408	0.432	0.160
109	0.687	0.407	0.439	0.154
108	0.694	0.403	0.448	0.149
107	0.700	0.400	0.456	0.144
106	0.707	0.396	0.465	0.139
105	0.713	0.392	0.474	0.134
104	0.719	0.387	0.483	0.130
103	0.725	0.383	0.492	0.125
102	0.732	0.379	0.500	0.121
101	0.738	0.375	0.508	0.117
100	0.744	0.370	0.518	0.112
99	0.750	0.366	0.527	0.107

$[\alpha]^{20}_{D\,386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
98	0.757	0.361	0.537	0.102
97	0.763	0.356	0.546	0.098
96	0.769	0.350	0.556	0.094
95	0.775	0.345	0.565	0.090
94	0.781	0.341	0.574	0.085
93	0.787	0.336	0.583	0.081
92	0.793	0.331	0.592	0.077
91	0.799	0.326	0.601	0.073
90	0.805	0.320	0.610	0.070
89	0.810	0.314	0.620	0.066
88	0.816	0.308	0.629	0.063
87	0.822	0.302	0.638	0.060
86	0.828	0.295	0.649	0.056
85	0.834	0.288	0.658	0.054
84	0.839	0.282	0.667	0.051
83	0.844	0.275	0.677	0.048
82	0.850	0.267	0.688	0.045
81	0.856	0.259	0.698	0.043
80	0.862	0.251	0.709	0.040
79	0.867	0.243	0.719	0.038
78	0.872	0.234	0.730	0.036
77	0.878	0.225	0.741	0.034
76	0.884	0.217	0.751	0.032
75	0.889	0.208	0.762	0.030
74	0.895	0.200	0.772	0.028
73	0.901	0.191	0.783	0.026
72	0.906	0.182	0.794	0.024
71	0.911	0.173	0.805	0.022
70	0.916	0.163	0.817	0.020
69	0.921	0.153	0.828	0.019
68	0.926	0.143	0.839	0.018
67	0.932	0.134	0.850	0.016
66	0.937	0.125	0.861	0.014
65	0.942	0.115	0.872	0.013
64	0.947	0.105	0.883	0.012
63	0.952	0.095	0.895	0.010
62	0.957	0.085	0.906	0.009
61	0.962	0.075	0.917	0.008
60	0.967	0.065	0.927	0.008
59	0.972	0.055	0.938	0.007
58	0.977	0.045	0.949	0.006
57	0.982	0.035	0.960	0.005
56	0.987	0.025	0.971	0.004
55	0.992	0.015	0.982	0.003
54	0.997	0.005	0.993	0.002
53.5	1.000	0.000	1.000	0.000

It would seem obvious that we are now prepared to determine whether a sample of glucose is a product of one hydrolysis or is a mixture of two separately converted products, by comparison of the actual analytical results with those calculated from the rotatory power.

For testing this method we have made a few analyses of commercial glucoses obtained in open market.

In the manufacture of glucose syrup all the starch is not hydrolyzed under strictly the same conditions, as the factory practice is to pump the starch into the converter, which is under steam pressure and already contains the hydrolyzing acid. As the filling of a converter takes about one-third of the total time of cooking, it is clear that there is a radical difference in the time of hydrolysis of different portions of starch. Nevertheless, we have found that samples known to have been made under these conditions conform to the laws of our curve, and the evidence seems strong that those which depart widely from these conditions are mechanical mixtures.

The following determinations of four samples of commercial glucose giving the cupric reducing power as found and as calculated for the corresponding rotation will illustrate the method:

Sample.	α_{D386}.	K_{386} (obtained).	K_{386} (calculated).
I. C. Pope Co. (J)·····	131.1	0.566	0.537
II. C. Pope Co. (M)····	125.4	0.578	0.578
III. Rockford Co ·······	141.9	0.454	0.457
IV. Chicago Co·········	137.2	0.505	0.495

Evidently II and III are normally hydrolyzed. IV is possibly a mixture, while I is undoubtedly so. As this latter is a sample of jelly goods which in factory practice are often made by mixing two lots, our conclusion is strengthened.

From the results as a whole we have concluded that the evidence is strong, (1) that in any homogeneous acid-converted starch product, irrespective of the conditions of hydrolysis, the specific rotatory power always represents the same chemical composition.

(2) That but three simple carbohydrates,[1] possible in molecular aggregates, exist in the solution of a starch product hydrolyzed by acids.

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[1] Leaving out of consideration the possible small amounts of products formed by reversion.

DETERMINATION OF THE CONVERSION OF COMMERCIAL GLUCOSE.

In the manufacture of glucose it is obviously essential to have a rapid means of determining the degree of conversion of the starch during the cooking process. The usual factory practice is to control the conversion by means of iodine color tests. These tests are usually made by adding a definite number of drops of standard iodine solution to a test-tube of the cooled glucose liquor. The tint at which the conversion is considered complete varies in general practice from that corresponding to $[\alpha]_D = 128$ to $[\alpha]_D = 135$, the variation being even greater in some cases, depending on the ideas of the manufacturer and the grade of goods desired.

By daily practice workmen become quite expert in making these iodine tints, which are usually carried out by crude methods and read off without comparison with any standard. Nevertheless, the product, when examined by more refined laboratory processes, shows wide variations from day to day, which does not appear surprising when we examine into the errors of such color tests.

Assuming that the test is carried out under uniform conditions of concentration and proportion of reagent to liquor to be tested, which is by no means always the case, the other conditions affecting the color are (1) temperature, (2) turbidity, and (3) illumination.

Uniform temperature can be obtained easily by some simple cooling device as a stream of running water.

The acid converter liquors are always turbid when tested, as filtration in this rapid testing is impracticable. The turbidity, however, is fairly constant. It is the third condition, that of illumination, which is constantly variable and which gives rise to the greatest error. This source of error can be largely eliminated by the use of a comparison standard, prepared of the same volume as that used in the color test and hermetically sealed in a glass tube of the standard size used in testing. Mixtures of solutions of iron salts with finely pulverized glass giving the requisite turbidity when shaken, can be easily made to exactly match the iodine tint, and will preserve their intensity indefinitely. When properly adjusted by means of polariscopic tests such standards have served well to fix the point of conversion within narrow limits and have done much to insure a uniform product.

It is of course important that these should be in the hands of the chemist or superintendent of the works, a much more exact means of testing the degree of conversion. This is most naturally accomplished by determining the specific rotatory power.

We have arranged a table for quickly calculating specific rotatory power, and found it so useful that we venture to publish it. The following simple calculation will sufficiently explain the principles on which the table has been worked out:

TABLE D.

TABLE FOR DETERMINING SPECIFIC ROTATORY POWER OF SOLUTIONS OF 7.50°–10° BRIX BY READING OF VENTZKE SACCHARIMETER.

Brix.	Sp. gr.	W = gram per 100 cc.	Log $\frac{17.20}{W}$	Brix.	Sp. gr.	W = gram per 100 cc.	Log $\left(\frac{17.20}{W}\right)$.
7.50	1.0298	7.724	0.3477	8.80	1.0352	9.110	0.2760
7.55	1.0300	7.777	0.3447	8.85	1.0354	9.163	0.2735
7.60	1.0302	7.829	0.3418	8.90	1.0356	9.217	0.2709
7.65	1.0304	7.883	0.3388	8.95	1.0358	9.270	0.2684
7.70	1.0306	7.936	0.3359	9.00	1.0360	9.324	0.2657
7.75	1.0308	7.989	0.3330	9.05	1.0362	9.378	0.2634
7.80	1.0310	8.042	0.3301	9.10	1.0364	9.430	0.2610
7.85	1.0312	8.096	0.3272	9.15	1.0366	9.484	0.2585
7.90	1.0315	8.149	0.3244	9.20	1.0368	9.538	0.2560
7.95	1.0317	8.202	0.3216	9.25	1.0370	9.592	0.2536
8.00	1.0319	8.255	0.3187	9.30	1.0372	9.646	0.2510
8.05	1.0321	8.308	0.3160	9.35	1.0374	9.690	0.2488
8.10	1.0323	8.361	0.3132	9.40	1.0376	9.753	0.2464
8.15	1.0325	0.415	0.3104	9.45	1.0378	9.807	0.2440
8.20	1.0327	8.468	0.3077	9.50	1.0381	9.862	0.2415
8.25	1.0329	8.522	0.3050	9.55	1.0383	9.916	0.2391
8.30	1.0331	8.575	0.3022	9.60	1.0385	9.970	0.2368
8.35	1.0333	8.629	0.2995	9.65	1.0387	10.023	0.2346
8.40	1.0335	8.682	0.2969	9.70	1.0389	10.077	0.2323
8.45	1.0337	8.735	0.2943	9.75	1.0391	10.130	0.2300
8.50	1.0339	8.788	0.2916	9.80	1.0393	10.185	0.2277
8.55	1.0341	8.842	0.2889	9.85	1.0395	10.239	0.2252
8.60	1.0343	8.895	0.2864	9.90	1.0397	10.293	0.2231
8.65	1.0345	8.949	0.2838	9.95	1.0399	10.347	0.2207
8.70	1.0347	9.002	0.2812	10.00	1.0401	10.401	0.2185
8.75	1.0350	9.056	0.2786				

Taking the usual formula for the specific rotatory power, $\alpha = \frac{av}{lw}$, where a is the angle of rotation of the solution of w

gram of the active substance in v cc. of water observed through a column l decimeters long. If we make $a = \alpha$ it is plain w is the weight of substance under standard conditions which will give a direct reading of the specific rotatory power without calculation. In an instrument reading in angular degrees under the usual conditions of $v = 100$ and $l = 2$, w is therefore $50\,g$.

If a is the reading of a saccharimeter with the Ventzke scale, $w = 50 \times 0.344 = 17.20$, and the specific rotatory power of any solution of known concentration of an optically active substance will be $\frac{17.2a}{w}$. The easiest way of finding the concentration of glucose solutions with sufficient exactness for this work is by the Brix (or Balling) hydrometer, as this instrument is now made of great accuracy.

Brix hydrometers are carried in regular stock of the larger houses dealing in chemical apparatus for brewers and sugar manufacturers, with scales having a range of about five degrees and easily read to 0.05 per cent. Thermometers are attached having corrections for temperature marked on the scale. Concentrations of about ten per cent. are most convenient for polarizing; hence a spindle will be needed reading from five to ten per cent.

The method of determining rotatory powers is as follows: The glucose is diluted to an approximately ten per cent. solution. An exact Brix (or Balling) reading is taken, corrected for standard temperature and the solution polarized in a 200 mm. tube in any saccharimeter with the Ventzke scale. The logarithm of the factor $\frac{17.20}{w}$ corresponding to the Brix reading is then found in the table. Therefore, the calculation which is, $\log\ [\alpha]_D = \log\ \left(\frac{17.20}{w}\right) + \log\ a$, simply requires finding the logarithm of the saccharimeter reading and the number corresponding to the sum of this and the logarithm given in the table. This number is the required specific rotatory power.[1]

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[1] Obviously a table made on the scheme of the well-known Schmitz table for cane-sugar syrups would do away with all calculation. Such a table is, however, rather bulky for insertion here.

Thus a solution of 7.85 Brix having a reading of 51.7°, Ventzke has the rotatory power of its anhydrous carbohydrates determined as follows:

By the table, the corresponding logarithmic factor is 0.3272.

$$\begin{array}{ll} \text{Log } 51.7 = & 1.7135 \\ \text{Factor} & \underline{0.3272} \\ & 2.0407 = \log 109.8 \end{array}$$

which is the required rotatory power.

In this calculation no correction is made for ash, which, as a rule, does not affect the results appreciably.

The errors due to the slight variations in the concentration of the solutions used and changes in the temperature of the laboratory are too small to be taken into consideration in factory work or in general commercial analysis. The method in practice is quite as rapid as the "quotient of purity" determination of cane-sugar syrups. We suggest that this, or some similar scheme, be uniformly used for expressing the results of all polarimetric investigations of honeys, syrups, and similar indeterminate mixtures of carbohydrates met with in commercial analysis, instead of merely giving the polarizations, or the specific rotatory powers referred to the weights of the sample. The advantages are obvious. Such analytical results would be close approximations to the exact specific rotatory powers of the mixed anhydrous carbohydrates, and would be convenient of interpretation by inspection as being directly comparable on what is for all practical purposes an absolute standard and the one used in all strictly scientific work of the kind.

THE SPEED OF THE HYDROLYSIS OF STARCH BY ACIDS.[1]

The laws of the speed of hydrolysis of the carbohydrates with the exception of that of cane-sugar have been but little studied. Solomon[2] has collected some data on the action of various acids at boiling temperature. Welhelmy[3] showed in the case of the catalytic action of hydrochloric acid on cane-sugar that if the

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[1] We are greatly indebted to Prof. A. A. Noyes, of this department, for valuable aid in calculating the results of this work on speed of hydrolysis.

[2] *J. prakt. Chem.*, (2), 28.

[3] *Ber. d. chem. Ges.*, 18, 2211.

amount of acid and the temperature remained constant the rate of the inversion at any specified moment is proportional to the amount of unchanged sugar present at that moment.

That is, if A_0 represent the amount of sugar originally present, x the amount of this sugar changed over in any period of time, t, and c the reaction-constant, we have $\frac{dx}{dt} = c\,(A_0 - x)$.

The relative values of the constant, c, of the various acids in their action on cane-sugar have been determined by several observers, notably Ostwald,[1] who has compared, by means of their constants, the relative effect of chemically equivalent quantities of a large number of acids, taking the constant of hydrochloric acid as a standard with the arbitrary value of 100.

Recent work shows that acids act on salicin,[2] one of the glucosides, in a manner analogous to that of cane-sugar, the speed of hydrolysis of this body by the different acids bearing the same relation to hydrochloric acid.

The observations noted above suggested the possibility that in the hydrolysis of starch the acids would show the same proportional speed of reaction. This is an especially interesting problem because the starch molecule is exceedingly complicated, the molecular weight being undoubtedly very high. Starch hydrolysis, however, must be considered as somewhat different from that of cane-sugar or salicin. While these are easily soluble in cold water, starch is totally insoluble at ordinary room temperature. On the other hand, amylodextrin, the product of decomposition of starch by boiling water, is somewhat soluble in cold water, its solubility increasing with rise of temperature.

As by the customary procedure in determining speed of hydrolysis, it would be necessary to ascertain the exact moment when all the starch has been converted into the soluble form, a point not conveniently determined, we have adopted a method of measurement, based on the following principles:

The conversion products of starch, with the possible exception of those of very high rotatory power, are easily soluble in water, and can be looked upon as mixtures of maltose, dextrose and dextrin.

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[1] *J. prakt. Chem.*, *1884*, 401.

[2] Noyes and Hall: *Ztschr. phys. Chem.*, *1895*, 240.

The starch first changes to amylodextrin. The hydrolysis then proceeds by successive stages through the so-called maltodextrin; maltose, and dextrose. "Reversion," so-called, may take place to some extent, a small amount of the dextrose forming dextrin-like bodies, "gallisin," "isomaltose," etc., but this point is not considered in this work. The dextrin may therefore be looked upon as the original substance hydrolyzed, and maltose and dextrose as successive products of the reaction.

Further, we have shown that whatever the condition of hydrolysis by acids, the specific rotatory power of any conversion product corresponds to a definite chemical composition, tables for determining which we have constructed.

Thus, for instance, a conversion product of 160° has been proved to contain 54.8 per cent. dextrin, the remainder being maltose and dextrose.

Hence, the time of taking any sample after the contents of the autoclave has acquired constant temperature, which requires about ten minutes, can be taken as the initial point for determining speed of hydrolysis, and all subsequent samples referred to this, as it is obvious that in any sample we can ascertain the dextrin unacted upon at that stage of the hydrolysis. The same holds true of maltose.

We have to deal with two reactions, the first being the hydrolysis of dextrin to maltose.

If A_0 is the amount of dextrin at the initial point taken, $A_0 - x$, the amount remaining at any time, t, and c the constant depending on conditions of hydrolysis we get, $\frac{dx}{dt} = c\,(A_0 - x)$.

This, on integrating, gives $\log \frac{A_0}{A - x} = ct$, or $\frac{1}{t} \log \frac{A_0}{A_0 - x} = c$, which is the general equation of a first-order reaction. The second decomposition is that in which maltose is hydrolyzed to dextrose, and is peculiar in so far as it proceeds simultaneously with that by which the maltose is formed. As a result of the hydrolysis of the dextrin the maltose increases rapidly to a maximum of 44.1 per cent. at a rotation of 129°.

It then gradually diminishes, while the dextrose percentage always increases.

Consequently, the equation expressing accurately the rate of change in the total amount of maltose present is quite complicated, and we have therefore used an approximate formula, which is sufficiently exact for the work in hand. The formula is derived from the exact differential equation

$$\frac{dD}{dt} = c_2 M,$$

which states that the amount of dextrose formed at each moment is proportional to the amount of maltose present by replacing the differential quantities by finite differences, which in applications of the formula must of course be taken small. In the place of M the average amount of maltose present during the interval of time considered is also substituted. That is, if M_1 and M_2 are the amounts of maltose present at the time, t_1 and t_2, and D_1 and D_2 the amounts of dextrose present at these same times, and c_2 is the reaction constant, we get as a result of the above mentioned substitutions:

$$D_2 - D_1 = c_2 \frac{M_1 + M_2}{2} (t_2 - t_1),$$

or,

$$\left(\frac{1}{t_2 - t_1}\right) \left(\frac{D_2 - D_1}{\frac{M_1 + M_2}{2}}\right) = c_2.$$

The results are contained in the following tables:

TABLE E.

SPEED OF HYDROLYSIS OF STARCH.

Hydrochloric acid: 0.02 normal; at 2 A $T = 135°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D\,386} = 161$; $A_0 = 55.8$.

Time t. (minutes)	$[\alpha]^{20}_{D\,386}$.	$A_0 - x$.	$\log \frac{A_0}{A_0 - x}$	C_1.	$\frac{D_2 - D_1}{\frac{m_1 + m_2}{2}}$	C_2.
10	137	35.5	0.2216	0.02216	0.3581	0.0358
20	118	20.3	0.4391	0.02196	0.3118	0.0312
30	100	11.2	0.6784	0.02261	0.3790	0.0379
40	88	6.3	0.9684	0.02421	0.3274	0.0327
50	76	3.2	1.2415	0.02483	0.4638	0.0464
60	69	1.9	1.4678	0.02446	0.4162	0.0416
70	64	1.2	1.6674	0.02382	0.4264	0.0426

$C_1 = 0.02344$. $C_2 = 0.0373$.

Sulphuric acid : 0.02 normal ; at 2 A $T = 135°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D\,386} = 177°$; $A_0 = 73.5$.

10	163	57.9	0.1036	0.01036	0.1954	0.0195
20	152	46.7	0.2248	0.01124	0.1436	0.0144
30	140	36.0	0.3100	0.01033	0.1703	0.0170
40	129	27.5	0.4270	0.01068	0.1678	0.0168
60	109	15.4	0.6788	0.01131	0.3656	0.0188
80	90	7.0	1.0212	0.01277	0.4700	0.0235
100	77	3.4	1.3348	0.01335	0.4809	0.0240
120	66	1.4	1.7202	0.01434	0.6915	0.0346

$C_1 = 0.0118$. $C_2 = 0.0211$.

Oxalic acid : 0.04 normal ; at 2 A $T = 135°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D\,386} = 180°$; $A_0 = 77.2$.

20	157	51.6	0.1750	0.00875	0.3147	0.0157
40	137	33.5	0.3626	0.00907	0.2890	0.0145
60	120	21.5	0.5552	0.00925	0.2738	0.0137
80	106	13.9	0.7446	0.00931	0.2762	0.0138
100	93	8.1	0.9791	0.00979	0.3224	0.0161
120	82	4.5	1.2344	0.00029	0.3426	0.0171
140	73	2.6	1.4726	0.01052	0.4149	0.0207

$C_1 = 0.00957$. $C_2 = 0.0159$.

Sulphurous acid : 0.02 normal ; at 2 A $T = 135°$ C.

$t_0 = 50$; $[\alpha]^{20}_{D\,386} = 187°$; $A_0 = 87$.

50	179	76.0	0.0587	0.00117	0.1254	0.00251
100	172	67.7	0.1089	0.00109	0.0907	0.00181
150	165	60.0	0.1613	0.00108	0.1012	0.00202
200	159	53.7	0.2095	0.00105	0.0799	0.00159
250	151	45.7	0.2796	0.00112	0.1036	0.00207
300	144	39.3	0.3451	0.00115	0.0978	0.00196
350	137	33.5	0.4145	0.00119	0.1053	0.00211
400	131	29.0	0.4773	0.00119	0.0893	0.00179

$C_1 = 0.00113$. $C_2 = 0.00198$.

Acetic acid : 0.5 normal ; at 2 A $T = 135°$ C.

$t_0 = 50$; $[\alpha]^{20}_{D\,386} = 170°$; $A_0 = 65.5$.

50	143	38.5	0.2307	0.00461	0.3775	0.00755
100	121	22.1	0.4718	0.00472	0.3516	0.00703
150	103	12.5	0.7193	0.00480	0.3643	0.00729
200	86	5.6	1.0680	0.00534	0.4638	0.00928
250	74	2.8	1.3690	0.00548	0.4969	0.00994

$C_1 = 0.00449$. $C_2 = 0.00822$.

Hydrochloric acid : 0.01 normal ; at 1 A $T = 121°$ C.

$t_0 = 40$; $[\alpha]^{20}_{D\,386} = 183°$; $A_0 = 81.3$.

40	168	63.3	0.1087	0.00272	0.2118	0.00529
70	158	52.7	0.1883	0.00269	0.1358	0.00453
100	149	43.8	0.2686	0.00269	0.1199	0.00400
140	137	33.5	0.3851	0.00275	0.1764	0.00441
180	126	25.5	0.5036	0.00280	0.1693	0.00423
200	120	21.5	0.5777	0.00289	0.1028	0.00514
250	107	14.4	0.7517	0.00301	0.2539	0.00508

$C_1 = 0.00279$. $C_2 = 0.00467$.

Hydrochloric acid: 0.01 normal; at 2 A $T = 135°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D_{386}} = 176°$; $A_0 = 72.3$.

10	162	56.9	0.1040	0.0104	0.1937	0.0194
20	148	42.9	0.2266	0.0113	0.1877	0.0188
40	128	26.8	0.4310	0.0108	0.3015	0.0151
60	110	16.0	0.6550	0.0109	0.3259	0.0163
80	93	8.1	0.9506	0.0119	0.4102	0.0205
100	81	4.3	1.2256	0.0123	0.3830	0.0182
120	70	2.0	1.5581	0.0130	0.4479	0.0294

$C_1 = 0.0115$. $C_2 = 0.0187$.

Hydrochloric acid: 0.01 normal; at 3 A $T = 145°$ C.

$t_0 = 10$; $[\alpha]^{20}_{D_{386}} = 174°$; $A_0 = 70$.

5	158	52.7	0.1233	0.0247	0.2766	0.0553
10	140	36.0	0.2888	0.0289	0.2528	0.0506
15	125	24.8	0.4506	0.0300	0.2351	0.0470
20	110	16.0	0.6410	0.0321	0.2756	0.0551
30	88	6.3	1.0458	0.0349	0.5544	0.0554
40	74	2.8	1.3979	0.0350	0.5630	0.0563
50	65	1.3	1.7212	0.0344	0.6349	0.0640

$C_1 = 0.0314$. $C_2 = 0.00548$.

Hydrochloric acid: 0.01 normal; at 4 A $T = 153°$ C.

$t_0 = 10$; $[\alpha]^{20}_{D_{386}} = 147°$; $A_0 = 42.0$.

5	117	19.7	0.3287	0.0657	0.4900	0.0980
10	96	9.4	0.6501	0.0650	0.4671	0.0934
15	79	3.8	1.0434	0.0696	0.5443	0.1088
20	68	1.8	1.3679	0.0684	0.6060	0.1212
25	61	0.85	1.6938	0.0678	0.7157	0.1431
30	57	0.5	1.9242	0.0641	0.7818	0.1564

$C_1 = 0.0668$. $C_2 = 0.1202$.

Hydrochloric acid: 0.04 normal; at 3 A $T = 145°$ C.

$t_0 = 5$; $[\alpha]^{20}_{D_{386}} = 150°$; $A_0 = 44.7$.

3	115	18.5	0.3831	0.1277	0.5736	0.1912
5	95	9.0	0.6961	0.1392	0.4541	0.2270
7	80	4.0	1.0481	0.1497	0.4833	0.2416
10	66	1.4	1.5042	0.1504	0.8083	0.2694
13	58	0.6	1.8721	0.1440	1.0350	0.3450
15	66	0.4	2.0482	0.1365	0.6285	0.3143

$C_1 = 0.1413$. $C_2 = 0.2648$.

Hydrochloric acid: 0.02 normal; at 3 A $T = 145°$ C.

$t_0 = 10$; $[\alpha]^{20}_{D_{386}} = 148°$; $A_0 = 42.9$.

5	116	19.1	0.3515	0.0703	0.5246	0.1089
10	96	9.4	0.6594	0.0659	0.4478	0.0896
15	80	4.0	1.0304	0.0687	0.5075	0.1015
20	69	1.9	1.3537	0.0677	0.5889	0.1178
25	61	0.85	1.7031	0.0681	0.7739	0.1548
30	56	0.45	1.9793	0.0660	1.0800	0.2160

$C_1 = 0.0678$. $C_2 = 0.1304$.

Hydrochloric acid: 0.01 normal; at 3 A $T = 145°$ C.

$t_0 = 5$; $[\alpha]^{20}_{D_{386}} = 174°$; $A_0 = 70$.

5	158	52.7	0.1233	0.0247	0.2766	0.0553
10	140	36.0	0.2888	0.0289	0.2528	0.0506
15	125	24.8	0.4506	0.0300	0.2351	0.0470
20	110	16.0	0.6410	0.0321	0.2756	0.0551
30	88	6.3	1.0458	0.0349	0.5544	0.0554
40	74	2.8	1.3974	0.0350	0.5630	0.0563
50	65	1.3	1.7212	0.0344	0.6349	0.0640

$C_1 = 0.0314$. $C_2 = 0.0548$.

Hydrochloric acid: 0.005 normal; at 3 A $T = 145°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D_{386}} = 172°$; $A_0 = 67.7$.

20	142	37.6	0.2554	0.0128	0.4270	0.0214
40	113	17.4	0.5901	0.0148	0.4900	0.0245
60	91	7.3	0.9673	0.0161	0.5226	0.0261
80	77	3.4	1.2991	0.0162	0.5082	0.0254
100	66	1.4	1.6845	0.0168	0.7429	0.0371
120	59	0.7	1.9855	0.0165	0.8172	0.0409

$C_1 = 0.0155$. $C_2 = 0.0279$.

At the head of each table are given data as to the concentration and nature of the acid, the temperature corresponding to the steam pressure given in atmospheres and $[\alpha]^{20}_{D_{386}}$ at the initial time period t_0 with the corresponding value of A_0. Time values are expressed in minutes, and the constants c_1 for the hydrolysis of dextrin, c_2 for that of maltose, are calculated according to the formulas given above.

The results show that the constants in general are satisfactory, and that therefore the reaction like the sucrose inversion follows the law of the first order. It will also be seen that the values c_1 are much more uniform than those of c_2, which is to be expected since c_1 is absolute and c_2 only approximate. Deviations of c_1 may be fairly ascribed to variations in temperature which, though slight, are significant, owing to the high temperature coefficient of the reaction.

The dextrin values in Table C are consequently correct within the limits of error of analysis. It will be seen that the values of c_2 are much more constant in those determinations in which t is larger and the values of $[\alpha]_D$ decrease slowly. This was to be expected from the conditions of the approximate formula given above for the decomposition of maltose, these requiring that the amount of substance changed in a period of time must be small. The question of reversion may possibly have some influence on the values of c_3 but as yet we are not prepared to express ourselves definitely on this subject.

The relative effects are shown in the following table: Table I shows the influence on the speed of hydrolysis of various acids at the same temperature, 135° C.

Table II shows the influence of temperature on the speed of hydrolysis when the same amount of acid is used.

Table III gives the influence of varying amounts of acid.

The mean value of constants are given in column II. Column III gives the relative value of the constants referred to that of $\frac{1}{100}N$ hydrochloric acid at 135° taken as 100. Column IV gives the velocity constants determined by Ostwald[1] for cane-sugar inversion by the same acids at half-normal concentration.

TABLE I.

Acid.	Concentration.	II.	III.	IV.
Hydrochloric	0.02 N	0.02344	100	100
Sulphuric	0.02 N	0.0118	50.35	53.6
Oxalic	0.04 N	0.00957	40.83	....
(")	(0.02 N)	(0.00479)	(20.42)	18.6
Sulphurous	0.02 N	0.00113	4.82	....
Acetic	0.5 N	0.00499	21.29	....
(")	(0.02 N)	0.00020	0.8	0.4

TABLE II.

Acid.	Concentration.	Temp.	I.	II.
Hydrochloric	0.01 N	121	0.00279	11.91
"	0.01 N	134	0.0115	49.07
"	0.01 N	145	0.0314	13.40
"	0.01 N	153	0.0668	28.50

TABLE III.

Acid.	Concentration.	II.	III.
Hydrochloric	0.04 N	0.1413	602.9
"	0.02 N	0.0678	289.3
"	0.01 N	0.0314	134.0
"	0.005 N	0.0155	66.13

It is seen that the corresponding numbers of columns III and IV agree fairly well. The relative influence of the various acids upon the hydrolysis of starch, sucrose and salicin are therefore nearly identical. It should be noted however that the chemical activity of hydrochloric acid on starch, as in the case of salicin

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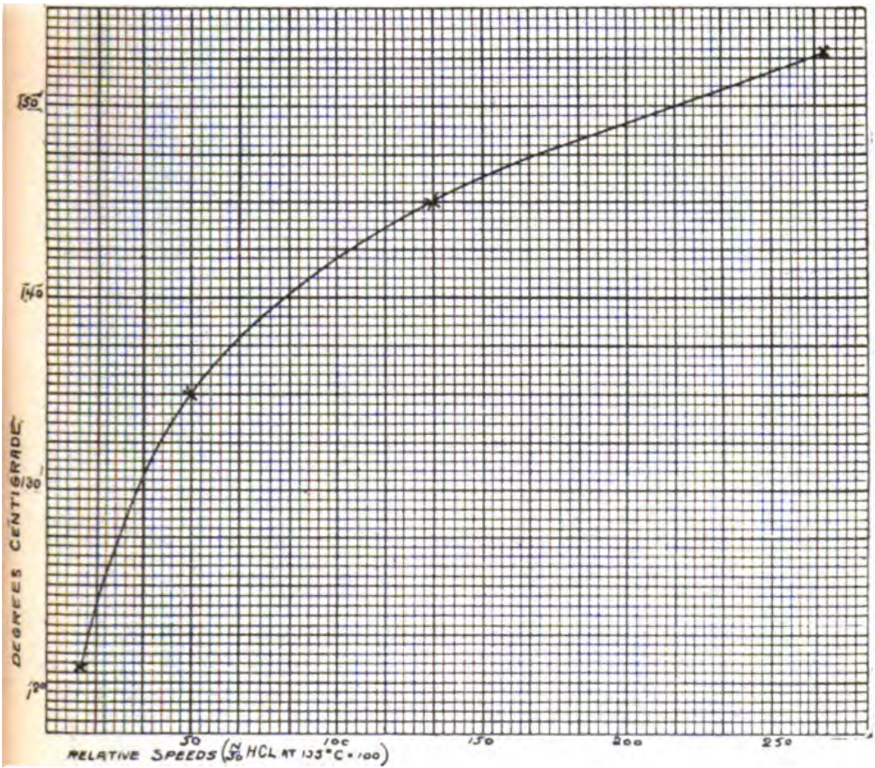
[1] *Loc. cit.*

and cane-sugar, increases in a greater ratio than the concentration, while the electrical conductivity increases more slowly.

The influence of temperature can be explained graphically by a curve approximating a parabola.



INFLUENCE OF TEMPERATURE

PLATE I.

Plate II shows the influence of the various acids.

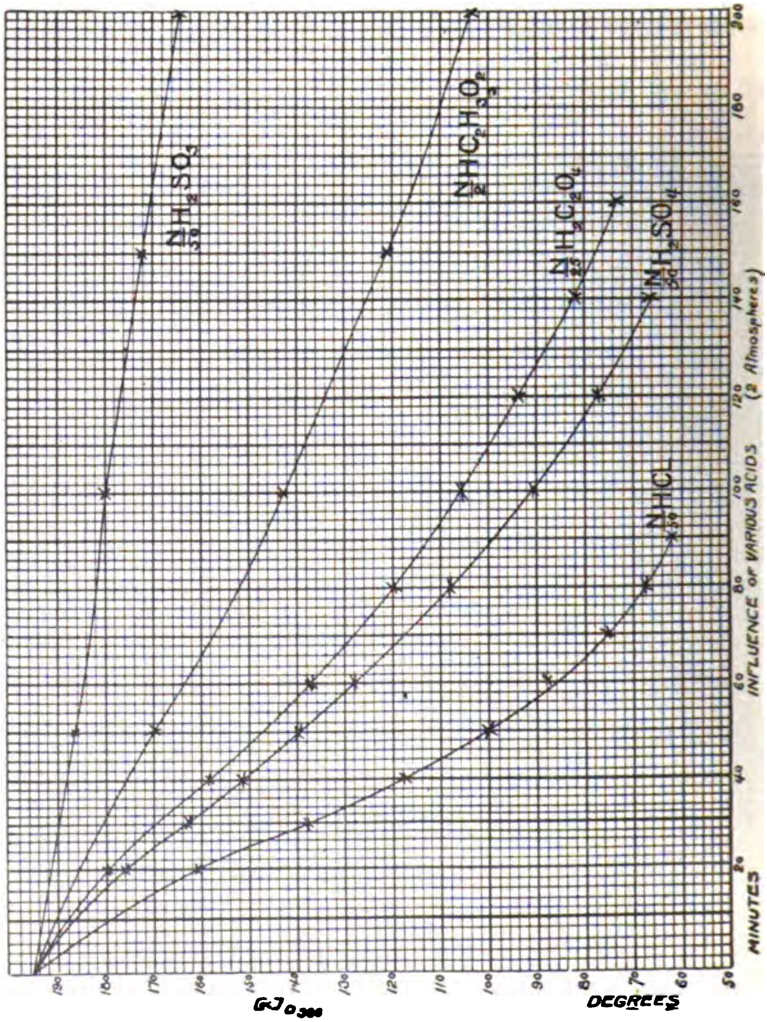


PLATE II.

Plate III shows the influence of the concentration, or amount of acid used.

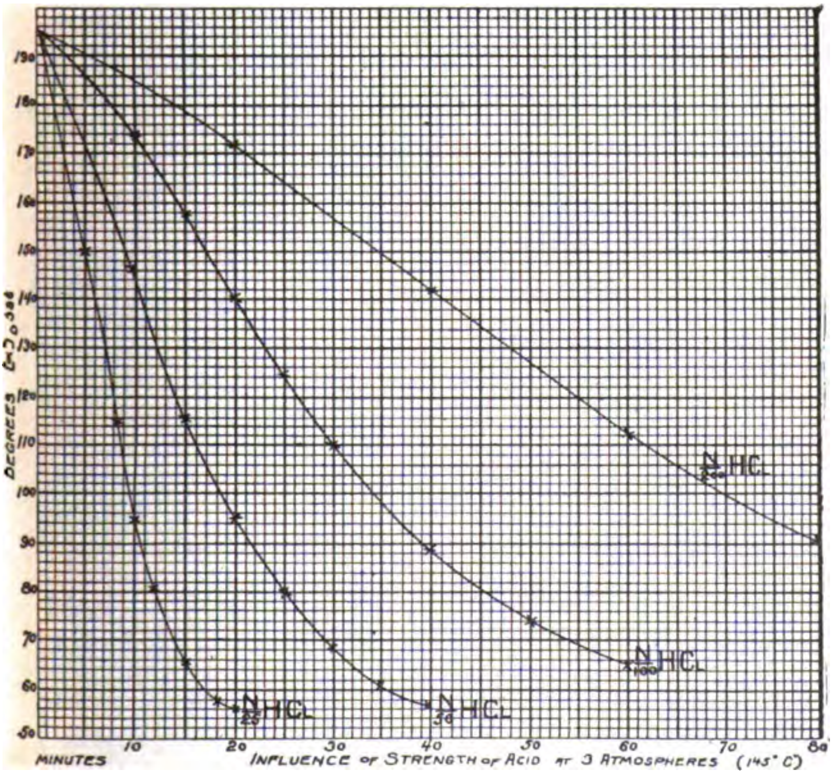


PLATE III.

Plate IV shows the relative curves due to temperature.

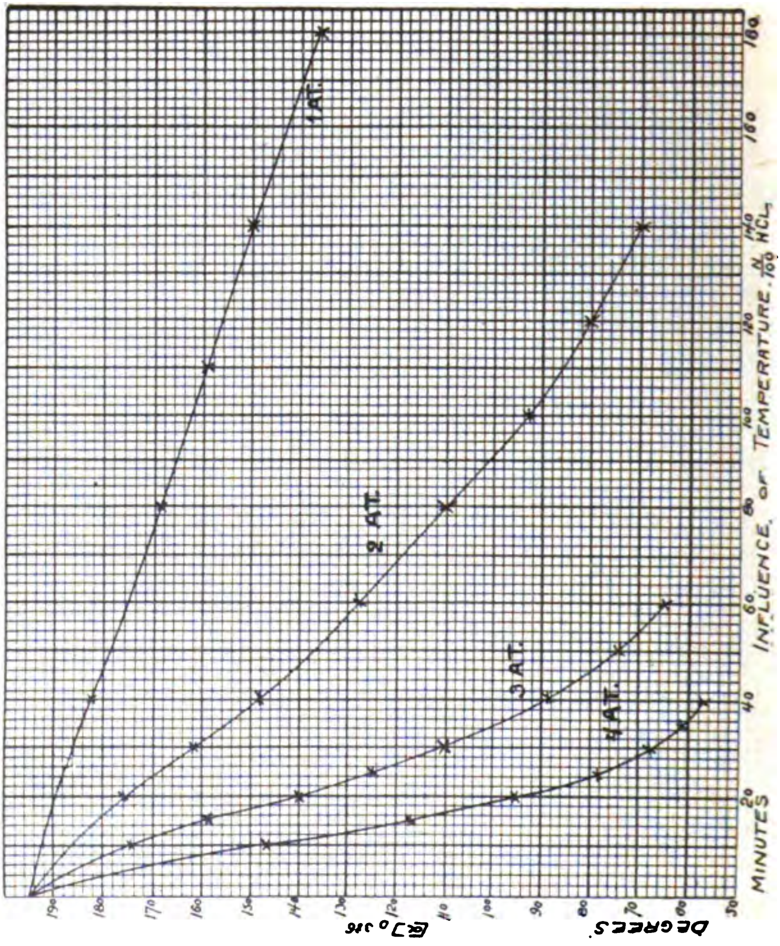


PLATE IV.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.

NICKELO-NICKELIC HYDRATE, $Ni_3O_4.2H_2O$.

BY WILLIAM L. DUDLEY.

Received August 26, 1896.

IN studying the action of fused sodium dioxide on metals, I have obtained interesting crystalline compounds, some of which, at least, have never been described. Only one of them has been carefully investigated and it proves to be nickelo-nickelic hydrate, having the formula $Ni_3O_4.2H_2O$.

It is prepared by fusing sodium dioxide in a nickel crucible with metallic nickel at a cherry-red heat. The action of the oxide upon the nickel proceeds with moderate rapidity, and in a few minutes scaly crystals appear floating in the fused mass. The crystals multiply steadily until, in the course of an hour, the contents of the crucible is thick with them, and comparatively little liquid remains. After cooling, the crucible is submerged in a beaker of distilled water and the undecomposed sodium dioxide together with the sodium oxide dissolves out, leaving the crystals which rapidly settle to the bottom of the liquid. The crystals should be washed several times with boiling water by decantation, and finally thrown in a filter. It is quite difficult to wash out all of the alkali, which adheres with unusual persistence. Probably the best plan to adopt is to put the crystals in a Soxhlet extraction apparatus and wash with water until no coloration is obtained with phenolphthalein. This requires about fifty hours of continuous washing. The crystals should then be dried at 110° C. and a magnet passed carefully through them to remove any particles of metallic nickel which may have eroded and not been completely acted upon.

The crystals are lustrous and almost black, with a slight brown-bronze hue. They are soft, and grind in a mortar much like graphite. The crystals seem to be hexagonal plates, but measurements of the angles have not been made. They dissolve slowly in acids, forming nickelous salts. Hydrochloric acid evolves chlorine; sulphuric and nitric acids, oxygen. They are insoluble in water and in solutions of the alkalies. The compound is not magnetic. The specific gravity is 3.4115 at 32° C.

At 130° C. the compound does not undergo decomposition, but at about 140° C. it begins to lose weight; at 240° C. the weight remains constant. At a red heat further loss is sustained and the residue remaining is nickelous oxide. The loss from 130° C. to 240° C. is due to water driven off, and at a red heat this loss is due to the evolution of oxygen.

The compound proved to be $Ni_3O_4.2H_2O$, as is shown by the results of the analysis:

Loss of H_2O on heating from 130° C. to 240° C.:

	Per cent.
First determination	13.00
Second "	13.13
Theory for $Ni_3O_4.2H_2O$	13.06

The residue remaining after heating to 240° C. is Ni_3O_4. On heating this residue to redness the loss of oxygen was found to be:

	Per cent.
Loss of oxygen	6.63
Theory	6.67

The total loss of water and oxygen obtained on heating the compound from 130° C. to redness was:

	Per cent.
First determination	18.91
Second "	18.88
Theory for $Ni_3O_4.2H_2O$	18.86

The oxygen given off on heating to redness was determined by calcining the compound in an atmosphere of carbon dioxide and collecting in Schiff's apparatus over potassium hydroxide solution. The result gave:

	Per cent.
Oxygen	5.93
Theory for $Ni_3O_4.2H_2O$	5.84

The nickel was determined and found to be:

	Per cent.
Nickel	63.67
Theory	63.72

In all of the calculations the atomic weight of nickel was taken to be 58.56 and oxygen 16.

The compound made in a nickel crucible of commerce is not perfectly pure, as the sample obtained was found to contain 0.71 per cent. of cobalt, the presence of which, however, would make no appreciable difference in the results of the analyses. No method has been found for freeing the compound from this impurity, and it appears at present as if the only plan would be to use a chemically pure nickel crucible in making it, for no crucible will withstand the action of fused sodium dioxide. Porcelain, iron, silver, gold and platinum crucibles are rapidly attacked.

The presence of water in this compound seems curious, but it may be due to the presence of sodium hydroxide in the sodium dioxide. Again it may be due to the water added to dissolve the soluble residue from the crystals. The first explanation seems to be the more plausible since the crystals are formed in the mass while it is fused, and they are not produced upon the addition of the water. If such is the case it would seem that the water driven off between 130° C. and 240° C. is from the breaking down of a true hydrate, rather than the expulsion of water of crystallization.

A cobalto-cobaltic hydrate, $Co_3O_4.2H_2O$, has been described,[1] but it was obtained by exposing to moist air, Co_3O_4, prepared by heating cobalt carbonate. Ni_3O_4, prepared by heating nickelo-nickelic hydrate to 240° C. is hygroscopic and absorbs about seven and four-tenths per cent. of water from the air at 30° C., which is completely lost at 110° C., showing that no hydrate is formed under these conditions.

The study of the action of fused sodium dioxide on the metals will be continued here, and it is hoped that some more data can be contributed soon.

VANDERBILT UNIVERSITY.

TABLE OF FACTORS.

BY EDMUND H. MILLER AND J. A. MATHEWS.

Received August 6, 1896.

ATOMIC masses, based on O = 16, taken from an article by F. W. Clarke, this Journal, March, 1896.

	Required.	Factor.	Logarithm.
$AlPO_4$	Al.	0.221976	$\bar{1}.3463071$
	Al_2O_3.	0.418489	$\bar{1}.6216835$
Sb_2O_4	Sb.	0.790067	$\bar{1}.8976643$
Sb_2S_3	Sb.	0.714570	$\bar{1}.8540446$
As_2S_3	As.	0.609522	$\bar{1}.7849890$
$Mg_2As_2O_7$	As.	0.483268	$\bar{1}.6841870$
Ag_3AsO_4	As.	0.162234	$\bar{1}.2101418$
$BaSO_4$	BaO.	0.657088	$\bar{1}.8176234$

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[1] Genth and Gibbs: *Am. J. Sci.*, 23, 257.

	Required.	Factor.	Logarithm.
	SO_3.	0.342912	$\bar{1}.5351829$
	S.	0.137342	$\bar{1}.1378121$
Bi_2O_3	Bi.	0.896600	$\bar{1}.9525990$
$CaCO_3$	CaO.	0.560296	$\bar{1}.7484173$
$CaSO_4$	CaO.	0.411899	$\bar{1}.6147904$
	$CaCO_3$.	0.735145	$\bar{1}.8663731$
CO_2	C.	0.272893	$\bar{1}.4359916$
Cr_2O_3	Cr.	0.684791	$\bar{1}.8355581$
$3K_2SO_4.2CoSO_4$	Co.	0.141511	$\bar{1}.1507892$
CuO	Cu.	0.798995	$\bar{1}.9025440$
Cu_2S	Cu.	0.798644	$\bar{1}.9023531$
Fe_2O_3	Fe.	0.700076	$\bar{1}.8451446$
Fe	Fe_2O_3.	1.42842	0.1548554
	FeO.	1.28561	0.1091100
	Fe_3O_4.	1.38082	0.1401359
$PbCrO_4$	Pb.	.640500	$\bar{1}.8065193$
$PbSO_4$	Pb.	.682927	$\bar{1}.8343742$
$Mg_2P_2O_7$	P.	.278681	$\bar{1}.4451076$
	P_2O_5.	.638038	$\bar{1}.8048465$
	MgO.	.361962	$\bar{1}.5586631$
	$MgCO_3$.	.757343	$\bar{1}.8792934$
Mn_3O_4	Mn.	.720490	$\bar{1}.8576283$
$Mn_2P_2O_7$	Mn.	.387226	$\bar{1}.5879648$
$(NH_4)_2PtCl_6$	Pt.	.439205	$\bar{1}.6426669$
	N.	.063281	$\bar{2}.8012744$
	NH_3.	.076911	$\bar{2}.8859881$
	NH_4Cl.	.241235	$\bar{1}.3824396$
Pt from $(NH_4)_2PtCl_6$	N.	.144081	$\bar{1}.1586075$
	NH_3.	.175114	$\bar{1}.2433212$
	NH_3Cl.	.549253	$\bar{1}.7397727$
K_2PtCl_6	KCl.	.306951	$\bar{1}.4870695$
	K_2O.	.193944	$\bar{1}.2876767$
KCl	K_2O.	.631840	$\bar{1}.8006072$
K_2SO_4	K_2O.	.540593	$\bar{1}.7328706$
SiO_2	Si.	.470199	$\bar{1}.6722814$
AgBr	Br.	.425560	$\bar{1}.6289611$
AgI	I.	.540313	$\bar{1}.7326479$
AgCl	Cl.	.247262	$\bar{1}.3931579$
	Ag.	.752738	$\bar{1}.8766436$
NaCl	Na_2O.	.530769	$\bar{1}.7249057$
Na_2SO_4	Na_2O.	.436801	$\bar{1}.6402836$
SnO_2	Sn.	.788150	$\bar{1}.8966087$
TiO_2	Ti.	.600749	$\bar{1}.7786928$
ZnO	Zn.	.803464	$\bar{1}.9049663$
$Zn_2P_2O_7$	Zn.	.429115	$\bar{1}.6325737$
$ZnNH_4PO_4$	Zn.	.366438	$\bar{1}.5640011$

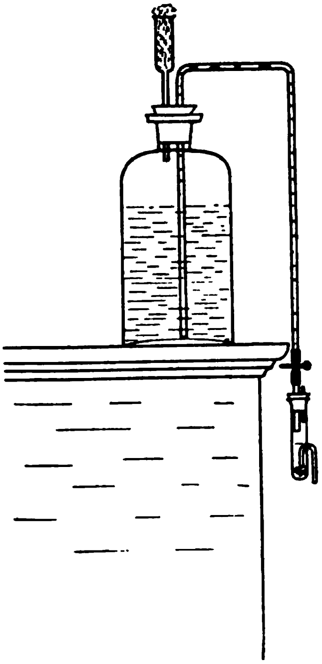
RAPID MEASURING PIPETTE.

BY EDWARD L. SMITH.

Received August 4, 1896.

THE apparatus described below is a device for rapidly measuring and discharging a definite volume of liquid. It may be well to state at this point that the principle is not applicable in all, or in even the majority of cases, where it is desired to measure and discharge liquid reagents in the laboratory. Where extreme accuracy is essential, the ordinary pipette or a burette must still be used. Perhaps the best way to explain the utility of the apparatus will be to state the exact use to which it is put in our laboratory. In the course of some experiments with sand filters, samples of the different effluents as well as of the applied sewage were taken daily, treated with a small quantity of a concentrated sterilizing agent, and an analysis made each week of the combined daily samples.

It was to measure and discharge this sterilizing solution that the apparatus was devised. The quantity added in each case was five cc. Of course a variation from that amount of one- or two-tenths cc. would not materially affect the results and the great advantage in convenience and rapidity over the use of the common pipette for the same purpose is admitted by all who have seen the apparatus work. A large bottle forms the reservoir. The stopper of this bottle carries two tubes. One simply serves to admit air and contains a loose plug of cotton to exclude dust, etc. The other tube is bent to form an ordinary siphon and the end of the longer limb is attached to a short glass tube by means of a rubber connection,



provided with a pinch-cock. The short glass tube to which reference was just made passes through a stopper inserted into the mouth of an ordinary test-tube. Through a hole blown in the side of this tube another glass tube, bent to form a siphon, is inserted and fastened in place by a piece of rubber tubing of the proper size, slipped on over the tube. The leg of the siphon inside the test-tube is of such a length that when the pinch-cock above is opened and the liquid allowed to enter the test-tube, five cc. will be automatically discharged when the level of the liquid has reached a mark on a line with the top of the bend in the siphon tube.

The apparatus can be constructed in a few moments in any laboratory, and for purposes to which it is adapted, it will, I am sure, be found satisfactory. It may be asked, what is the advantage of the form suggested over the ordinary burette with supply tubes? The answer is, it does away with the necessarily oft-repeated filling of the burette, and there is but one mark to watch in making the measurement—that previously mentioned, on the test-tube. The tubing used is of such size that a rapid discharge is insured, the time required being less than would be the case were a burette employed.

MERCURIC CHLOROTHIOCYANATE.

By Charles H. Herty and J. G. Smith.

Received August 8, 1896.

It has been shown by one of us[1] that the so-called compound lead iodochloride, PbICl, is not a true chemical compound, but a mixture of lead iodide and lead chloride.

It has seemed advisable, therefore, to study more fully the nature of the compound mercuric chlorothiocyanate, HgCl(CNS), described by McMurtry.[2] To this end a series of solutions was prepared, in one of which was used the exact proportions of mercuric thiocyanate and mercuric chloride given by McMurtry for the preparation of mercuric chlorothiocyanate; in the other members of the series, arbitrarily taken quantities of the one salt were replaced by equivalent quantities of the other. The

[1] *Am. Chem. J.*, 18, 290.

[2] *J. chem. Soc.*, *1889*, 50.

mixed salts were completely dissolved in hot water and the solutions allowed to cool and crystallize. The quantities actually used were :

Name.	Mercuric thiocyanate. Grams.	Mercuric chloride. Grams.	Water. cc.
A	9.5000	3.1439	2000
B	6.7500	65.5004	750
C	5.5000	6.5715	550
D (McMurtry)	5.0000	7.0000	450
E	4.5000	7.4285	350
F	3.5000	8.2853	300
G	1.0000	10.4296	200

On cooling, crystals separated from all of the solutions except *G*. The crystals from *A*, *B*, *C*, and *D* were fern-shaped, while those from *E* and *F* were prismatic.

By evaporating the solution *G* one-half, quite a good crop of prismatic crystals was obtained. The crystals from all of the solutions were separated from the mother-liquor by filtration and rapid pressing between folds of drying paper.

From the mother-liquor of *D* two crops of prismatic crystals were obtained by evaporating to one-half and then to three-fourths of original volume. These were designated *D'* and *D''*.

The character of the various crops of crystals was determined by estimating the mercury present in each. This was done by reducing the compounds with sodium peroxide, as recommended by Schuyten,[1] and weighing the mercury. Analysis showed :

		Mercury calculated for		
	Mercury found, per cent.	Mercuric thiocyanate, per cent.	Mercuric chlorothiocyanate, per cent.	Mercuric chloride, per cent.
A	62.72	63.28	68.12	73.85
B	62.76	....	....	....
C	62.74	....	....	....
D	63.91	....	....	....
E	68.24	....	....	....
F	68.67	....	....	....
G	72.59	....	....	....
D'	....	68.45	....	....
D''	....	....	72.41	....

These results show that the various crops of crystals fall into three classes, mercuric thiocyanate, mercuric chlorothiocyanate, and mercuric chloride. This was confirmed by inspection with

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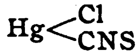
[1] *Chem. Ztg.*, 20, 239.

the microscope. Further, the three successive crops of crystals from solution *D* are seen to be the first mercuric thiocyanate, slightly contaminated by mercuric thiocyanate, as proved both by the high analytical result and by microscopic inspection, the second crop is mercuric chlorothiocyanate, and the third mercuric chloride.

The low results in the case of the pure salts is undoubtedly due to the fact that the filters containing the reduced mercury were dried at the ordinary temperature with consequent slight volatilization of mercury.

The effect of crystallization upon the salt mercuric chlorothiocyanate was next tried. A portion of the salt was dissolved in hot water just sufficient for complete solution. On cooling crystals separated, which, under the microscope, were seen to be only mercuric thiocyanate. The mother-liquor from these, on evaporating one-half, yielded only mercuric chlorothiocyanate. On evaporating the mother-liquor from this last two-thirds the crystals formed are seen to be a mixture of crystals of mercuric chlorothiocyanate and mercuric chloride. Finally, on evaporating this mother-liquor to dryness spontaneously, only crystals of mercuric chloride were obtained. The substance therefore undergoes dissociation when dissolved in water.

From all of the above it would seem that mercuric chlorothiocyanate is a true chemical compound, and further, that the only compound which can be prepared from solutions of mercuric chloride and mercuric thiocyanate is that represented by the formula  $Hg<^{Cl}_{CNS}$ or $HgCl_2.Hg(CNS)_2$.

These results varying so widely from those obtained in the case of lead iodochloride suggest the question: is the difference due to the fact that in the one case we have the more closely related groups, iodine and chlorine, while in the other we have the more different groups, thiocyanogen and chlorine, or is the difference due to the fact that in the one case we have a lead compound while in the other a mercury salt? To test this point work will be begun at once on mixtures of lead chloride and lead thiocyanate.

UNIVERSITY OF GEORGIA.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.]

XXIV.—COMPOSITION OF AMERICAN KAOLINS.

BY CHARLES F. MABERY AND OTIS T. KLOOZ.[1]

Received July 22, 1896.

ALTHOUGH great advances have been made in recent years toward a better knowledge of American clays and suitable methods for the manufacture of ware from them, much more extended investigation is necessary, both concerning the composition of the great clay deposits and in the details of manufacture. The first and most essential information is a correct knowledge of the composition of all clays available for use. Of scarcely less importance is masterly skill in the purification of crude materials, shaping the ware and burning. In the preparation of materia lsit is questionable whether American manufacturers can wait patiently several months for the slow processes of lixiviations and kneading that European porcelain makers have found indispensable in the production of the finest porcelain. The great porcelain factories in Europe are founded on the application of scientific skill and a personality in shaping and burning, handed down by lineal descent through many generations. Is it possible to procure for American factories scions for those ancient families, or must we wait for its perfection by our own ready facility and ingenuity?

As already mentioned, the porcelain manufacturer must be perfectly familiar with the composition of all materials within his reach. In making suitable mixtures he must have before him as one of the most essential features of composition, the proportions of free and combined silica, as well as the percentages of lime, iron, alkalies and water.

Having at hand a collection of clays, including representatives of American deposits, as well as several specimens from famous factories in Germany, it seemed of interest to compare the composition of clays from different sources. For the manufacture of the finest porcelain, the kaolin used in the Royal Berlin factory, at Charlottenburg, may be accepted as a standard of comparison. As every one knows who is familiar with the

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[1] This work was offered by Mr. Klooz in a thesis for the degree of Bachelor of Science.

qualities of true porcelain, the products from this factory are approached by no other in the world. The composition of the kaolin used in the manufacture of this ware is shown by the following analysis of the clay, two specimens selected at different times, from great quantities within the Berlin factory.

	I.	II.
Combined water	6.00	7.65
Silica	72.16	65.70
Alumina	20.05	24.49
Iron	0.10	1.03
Lime	1.14	0.60
Magnesia	0.02	0.26
Sodium oxide	0.12	0.23
Potassium oxide	0.41	0.03
Free silica	49.84	44.93

The different percentages in these analyses indicate that some latitude is permissible, although a high percentage of silica is evidently essential. These analyses show nearly the same composition as is given in the numerous analyses of the most celebrated clays of the German factories, especially in the low percentages of lime, iron and alkalies, and the large proportion of silica. An analysis of biscuit ware from the same factory shows nearly the same composition. Apparently the clay has the required proportion of silica without further addition :

Silica	68.24
Alumina	29.16
Iron	0.10
Lime	1.18
Magnesia	0.12
Alkalies	0.17
Free silica	57.50

Of the American clays, analyses showed that some contained a considerable excess of silica above the amount required for the oxygen ratio of silica to that of the alumina, 2 : 1, or the formula $Al_2O_3.3SiO_2$, which is accepted in the manufacture of the best German ware ; others only a small excess of silica. Of the high silica clays, a specimen from a deposit in Maryland gave the following results :

Combined water	11.23
Silica	47.60
Alumina	37.38
Iron	1.66
Lime	1.50
Sodium oxide	0.22
Potassium oxide	0.34
Free silica	17.10

Another clay of this class is a Missouri kaolin which was analyzed:

Combined water	4.15
Silica	82.64
Iron	12.41
Lime	0.05
Magnesia	0.11
Sodium oxide	0.08
Potassium oxide	0.53
Free silica	69.45

The following analysis represents another high silica clay from Black Rock, Arkansas:

Combined water	3.98
Silica	84.24
Alumina	11.50
Iron	0.08
Lime	0.52
Magnesia	0.02
Sodium oxide	trace
Potassium oxide	0.42
Free silica	69.93

Another high silica clay is from Milton Hollow, Middlesex Co., N. J.:

Combined water	5.52
Silica	75.06
Alumina	18.32
Iron	0.08
Lime	0.80
Magnesia	0.14
Potassium oxide	0.25
Free silica	59.71

A specimen of clay from a deposit in Washington, Middlesex Co., N. J., also showed a high percentage of silica:

Combined water	2.00
Silica	89.16
Alumina	5.77
Iron	0.07
Lime	0.70
Magnesia	0.12
Potassium oxide	1.29
Sodium oxide	1.31
Free silica	80.30

A clay having nearly the same composition as the specimen from the Berlin factory, is from a deposit at Hockessen, Delaware :

Combined water	6.55
Silica	71.46
Alumina	21.02
Iron	0.08
Lime	0.54
Magnesia	0.14
Potassium oxide	0.33
Sodium oxide	0.36
Free silica	53.13

It should not be inferred from the foregoing analyses that all American clays are high in silica. Some of the largest and most important deposits contain very little free silica. One of the purest kaolins is found in large quantities in Indiana, and the following analysis shows its composition :

Combined water	15.09
Silica	44.23
Alumina	40.56
Iron	0.07
Lime	0.13
Magnesia	0.10
Potassium oxide	0.10
Sodium oxide	0.15
Free silica	2.41

A clay of somewhat similar quality is found in Northampton Co., Pa. :

Combined water	11.20
Silica	48.16
Alumina	37.24
Lime	2.00
Magnesia	0.29
Iron	1.16
Potassium oxide	0.25
Sodium oxide	0.08
Free silica	2.85

A paper clay from South Amboy, N. J., Middlesex Co., gave the following results on analysis:

Combined water	13.35
Silica	43.30
Alumina	42.45
Iron	0.09
Lime	0.34
Magnesia	0.10
Potassium oxide	0.44
Sodium oxide	0.08
Free silica	3.55

A washed clay used in the manufacture of china, from New Castle, Del., gave the following composition :

Combined water	12.95
Silica	47.42
Alumina	38.42
Iron	0.08
Lime	0.70
Magnesia	0.12
Potassium oxide	0.30
Sodium oxide	0.12
Free silica	4.79

A clay in Woodbridge, Middlesex Co., N. J., also used in the manufacture of ware, is nearly pure kaolin:

Combined water	14.34
Silica	44.34
Alumina	38.09
Iron	0.15
Lime	0.96
Magnesia	0.10
Potassium oxide	1.00
Sodium oxide	0.79
Free silica	1.33

It is interesting to compare the composition of American kaolins with a standard kaolin used in England:

Combined water	13.00
Silica	46.00
Alumina	40.00
Iron	0.33
Lime	0.33
Magnesia	0.33

Several of the clays analyzed are used in the manufacture of ware. From some of these deposits specimens have been analyzed, and the results given in the "Chemistry of Pottery," by K. Langenbeck, are not essentially different from those given in this paper.

It is evident that the wide differences in the proportions of clay and silica in American kaolins render it imperatively necessary that they be taken into account in the selection of materials for the manufacture of ware. It is also evident that the United States is not wanting in an abundance of material for the manufacture of ware equal to the best foreign production.

DISCUSSION.

Wm. McMurtrie: It is an interesting fact not brought out here, that in many of the clays of New Jersey, and I think particularly from some of the deposits represented in the tables, Prof. Geo. H. Cook reported appreciable quantities of titanic oxide amounting to one-half per cent. more or less. The same constituent has been found in clays from other localities which I do not now exactly remember, but I have been led to believe that the existence of titanic oxide may be expected in a good many American clays.

W. A. Noyes: I have analyzed a number of Indiana clays and have found titanic oxide with but one exception. The Indiana clay given corresponds closely with one I analyzed last fall, and that particular one is free from titanic oxide, or practically so. All the other clays, and I feel safe to say that all these clays must contain titanic oxide.

The President: Does anyone know the effect of titanium on the ware?

A. A. Breneman: My impression is that Seger says there seems to be a connection between the peculiar light gray of salt-glazed stoneware, a color which is unique, and the presence of titanium. That is a very interesting statement, because that peculiar form of whitish or bluish gray stoneware is very characteristic, and I see nothing in the presence of iron alone in the clay sufficiently to account for it.[1]

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.]

XXV. COMPOSITION OF CERTAIN MINERAL WATERS IN NORTHWESTERN PENNSYLVANIA.[2]

BY A. E. ROBINSON AND CHARLES F. MABERY.

Received July 26, 1896.

THE therapeutic qualities of mineral springs throughout northwestern Pennsylvania have long been recognized, and recently some of these springs, notably those at Saegertown and Cambridgeboro, have come into prominence through the enterprise of persons interested in hotels and sanitariums. The desirable qualities of these waters are doubtless dependent on

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[1] NOTE ON TITANIUM IN CLAYS.—In the course of a discussion of Prof. Mabery's paper on American clays at the Buffalo meeting I alluded to the peculiar color of salt-glazed stoneware, and ascribed to Seger the suggestion that it was due to the presence of titanium. On referring to Seger's article (Wagner's Jahresbericht, 1883, p. 625), I find that he says that titanic acid (13.3 per cent.) heated with a very pure kaolin to a temperature between the melting points of wrought iron and platinum fuses, and that titanic acid is, under similar conditions, more of a flux for clay than silicic acid is. In the proportion of 6.65 per cent. of TiO_2, the mass became only semi-fused, and exhibited a dark-blue gray color. He says this color suggests the tint given by many clays when strongly heated.

Morgenroth (Wag. Jahr., 1884, 638) says, however, that rutile gives to clay ware a gray color under the glaze when impure ferruginous clays are used, but a yellow, ivory-like tint with pure clays. As rutile was used in the proportion of only 0.4 per cent., the minute proportion of iron which it carries (1.5 to 2.4 per cent. Fe_2O_3) would have little effect.

The interpretation of these facts to explain the peculiar gray color of salt-glazed stoneware, was probably a suggestion of my own, made at the time of reading these articles a dozen years ago. It was ascribed in the course of the discussion to Seger, as my "impression."

Nevertheless, in view of the peculiarity of this color, the gray of salt-glazed ware which is uniform throughout the body and becomes more bluish in overburned pieces, and in view also of the presence of iron in the rather crude clays used for the ware, and the fact that iron alone tends to escape as volatile chloride in presence of the salt used for glazing, the suggestion is worthy of note. A. A. BRENEMAN.

[2] This work, with a study of the methods of analysis, was offered by Mr. Robinson in a thesis for the degree of Bachelor of Science. Read at the Buffalo Meeting, August, 1896.

iron and certain other salts, especially on the bromides, and it is a popular view that lithium salts sometimes present impart valuable medicinal qualities. A quantity of water was collected from one of these surface springs at Conneautville by one of us (Robinson) and its composition as shown by analysis may serve as a representative of the springs in this region. The total solids in this water is equivalent to 6.586 grains per imperial gallon, or 9.83 parts per 100,000. Evidently the combination of bases and acids is to a certain extent arbitrary, but this distribution accounts for the total quantities of the various elements given by analysis:

	Grains per gallon.
Potassium carbonate	0.985
Lithium carbonate	0.002
Sodium chloride	0.925
Calcium bicarbonate	2.879
Calcium sulphate	1.291
Magnesium chloride	0.204
Ferrous carbonate	0.743
Silica	0.233
Hydrogen sulphide	trace

The specific gravity of this water was found to be 1.0002 at 20°. Evidently the analysis shows the composition of a good potable water. Any medicinal qualities it possesses must be referred to the iron and perhaps to a less extent to the lithium.

At greater depths in this section of Pennsylvania and in certain portions of Ohio, water may be found that partakes in a greater degree of the qualities imparted by the constituents of bittern. Wells sunk to depths of 1,000 to 3,000 feet have penetrated strata enclosing, frequently under great pressure, large quantities of bittern waters. While in general conforming in composition to the salts contained in bittern, occasionally these wells have yielded peculiar results on analysis. Such an aqueous stratum was reached several years ago at Conneautville, Crawford County, Pa., in an endeavor to obtain oil or gas. The drill penetrated the formation enclosing water at a depth of 2,667 feet and the drilling tools were forced upwards to a height of 1,800 feet by the water which prevented further drilling. This level was maintained notwithstanding vigorous attempts to clear the well by pumping. A slight examination then showed that this water possessed peculiar qualities, but the well received no further attention until within a few months ago when it was cleared and a quantity of the water was procured for a more thorough examination. The total solids is equivalent to 21,334.34 grains per gallon or to 30,536 parts per 100,000. The specific gravity of the water is 1.205 at 15°. Its composition as shown by the results of analyses is as follows:

	Grains per gallon.	Parts per 100.000.
Potassium chloride	528.577	755.6
Lithium "	56.422	80.3
Ammonium "	151.879	216.6
Sodium "	9902.578	14430.0
Potassium bromide	137.010	245.7
" iodide	2.078	2.96
Magnesium chloride	2172.499	3096.0
Calcium "	8335.537	11880.0
" sulphate	7.886	11.1
Ferrous carbonate	114.836	163.5
Aluminum chloride	21.816	31.1
Silica	3.220	4.6
Hydrogen sulphide	0.033	0.05

There are certain features of this water that deserve especial mention. The large proportion of ammonium chloride is quite unusual in waters from such depths. Lithium chloride is frequently found in surface springs, and in brines from deep wells, but rarely, if ever, in such quantities as this water contains. If lithium salts impart to spring water the therapeutic qualities claimed for them, it is not difficult to account for the beneficial effects that have been observed in the use of this water. No doubt the large proportion of potassium bromide has much to do with the marked sedative effect. The large percentage of potassium iodide is also phenomenal, and it must intensify the mineral characteristics of the water. Besides the characteristics of a bromo-lithia water the large percentage of iron assures the desirable qualities of an iron water. The peculiar composition of this water, especially in the large quantities of the rarer elements, offered a favorable opportunity to ascertain whether these bittern deposits contain also the elements, cesium and rubidium, which are rarely found in springs. Forty-five liters of the water were evaporated to a small volume, removing the great quantities of salt as they separated. When the volume was reduced to less than fifty cc. this solution as well as the lixiviated salts that had separated during evaporation were carefully examined in the spectroscope. But not a trace of rubidium nor cesium could be detected. It is therefore safe to conclude that the bittern deposits from the ancient sea do not contain these rarer elements.

It may not be out of place to remark that the chemical composition of this water explains the remarkable therapeutic qualities especially for rheumatism and nervous diseases that it has been found to possess.

SOME ANALYTICAL METHODS INVOLVING THE USE OF HYDROGEN DIOXIDE.[1]

By B. B. Ross.

Received August 31, 1896.

THE use of hydrogen peroxide as a laboratory reagent, although originally restricted to a few operations of minor importance, has within recent years met with a much wider extension, and its numerous applications in both qualitative and quantitative analysis, render it at present almost indispensable in every well-equipped analytical laboratory.

Among the more interesting applications of this substance in quantitative estimations are those which are based on the reaction which takes place when an excess of hydrogen dioxide is brought in contact with an acid solution of chromic acid, and Baumann[2] several years since described quite fully a number of analytical processes growing out of the reaction referred to.

In the process for the estimation of chromic acid in soluble chromates as outlined by Baumann, the substance under examination is first brought into a state of solution, and the not too concentrated liquid is transferred to a generating flask of special construction.

[1] Read at the Buffalo meeting, August 22, 1896.

[2] *Ztschr. anal. Chem.*, 31, 436.

Ten cc. of dilute sulphuric acid are next added, after which from five to ten cc. of commercial hydrogen peroxide are run in from a small closed vessel connected with the generating flask, while the oxygen which is evolved, after the vigorous shaking of the contents of the flask, is collected over water in an azotometer.

The following equations given by Baumann illustrate the chemical changes connected with the above described reaction :

$$K_2Cr_2O_7 + H_2O_2 + H_2SO_4 = K_2SO_4 + 2H_2O + Cr_2O_7 ;$$
$$Cr_2O_7 + 3H_2SO_4 + 4H_2O_2 = Cr_2(SO_4)_3 + 7H_2O + O_8.$$

From these equations it will be seen that for two molecules of chromic acid or one molecule of potassium dichromate, there are evolved eight atoms of oxygen, giving an equivalent of 445.3 cc. of oxygen (measured at 0° C. and 760 mm. pressure) for each gram of chromic acid which may be present.

The writer, soon after the appearance of the original article by Baumann, made a number of experimental tests of this method with a view to applying it to some other analytical processes, and still more recently has conducted a series of tests for the purpose of determining the adaptability of Baumann's method to the indirect volumetric estimation of iron.

In the dichromate method for the volumetric determination of iron, as commonly employed, the end point of the oxidation process is ascertained by the reaction with potassium ferricyanide.

As the end of this reaction is almost invariably difficult to determine particularly if zinc has been employed as a reducing agent, the dichromate process has met with but limited application.

In order to apply the principle of the chromic acid method of Baumann to the estimation of iron, an excess of dichromate solution was employed in all of the tests and experimental determinations, the amount of the excess of chromic acid being determined by the volume of oxygen evolved upon treatment with hydrogen dioxide.

The mode of procedure adopted was as follows :

A dichromate solution was prepared by dissolving 4.913 grams of C. P. crystallized potassium dichromate in water and diluting to a bulk of one liter.

The iron solution employed in standardizing the dichromate and permanganate solutions was obtained by dissolving iron wire in dilute sulphuric acid, the solution being reduced with metallic zinc, as usual, previous to titration.

The dichromate solution was also titrated against a freshly prepared solution of ammonium ferrous sulphate, the strength of which had been determined by titration with permanganate solution, which had also been carefully standardized by means of iron wire.

In order to ascertain the strength of the dichromate solution by the hydrogen dioxide method, about fifteen cc. of the dichromate solution is run into the generating flask above referred to, and there is also added an amount of ferric sulphate solution (free from ferrous sulphate) equivalent to about 0.06 to 0.10 gram of iron. The object of employing the ferric sulphate in this standardization is to supply approximately the same conditions as obtain in the process for the actual determination of iron.

The amount of oxygen given off from chromic acid in the presence of ferric sulphate is slightly less than that evolved when ferric sulphate is absent, but the amount of ferric iron present may vary considerably without affecting the volume of oxygen liberated.

To the contents of the generating vessel about ten cc. of dilute sulphuric acid are now added, and the flask is then connected by means of a rubber tube with a Schulze's azotometer, which has been filled with water to the zero point.

From five to ten cc. of hydrogen dioxide are next run in from a small closed vessel connected with the generating flask and the mixed liquid is then shaken, at first gently, and afterwards vigorously. The tube leading from the flask to the azotometer should be provided with a stop-cock, which should be closed before and opened immediately after each shaking.

The last trace of the oxygen liberated will not be disengaged until after the lapse of about five minutes, but it is not necessary to continue the shaking during the whole of this period. After equalizing the height of the water in the two tubes of the azotometer, the volume of oxygen is noted and is easily corrected for temperature and pressure by reference to proper tables.

In order to test the strength of the dichromate solution by means of iron wire, a given weight of the wire is dissolved in dilute sulphuric acid, the solution reduced with zinc, as usual, and rapidly transferred to the generating flask (filtering, if necessary).

An excess of dichromate solution is now run in, hydrogen dioxide is added, and the oxygen is set free and collected as before described.

If a large excess of dichromate has been used in the preliminary test, duplicate tests should be made with employment of a small excess, say from two to three cc., of the dichromate.

The strength of the solution can then be readily calculated by difference, and, if necessary, the results can be checked by still further tests.

In the determination of iron in ores by this process, the solutions of ferric iron are reduced by zinc, as in the common permanganate method, and the remainder of the process is conducted just as described for the standardization of the dichromate by means of iron wire.

In addition to numerous tests of solutions of pure iron, several estimations of iron in iron ores were made by this process, the results obtained being compared with those secured by the permanganate method.

The following are the results of the tests of the iron ores referred to:

	Permanganate method. Mean of several determinations.	Dichromate method.
Iron ore No. 1	40.92	40.59
		41.25
Iron ore No. 2	54.71	55.35
		55.43
		55.50

In the determination of iron in ores by this process, it is best, as in the case of the tests with iron wire, to employ only a small excess of the dichromate solution, after making a preliminary determination, as the results are much more accurate with a small than with a large excess of chromic acid.

While a sufficient number of determinations have not been made to ascertain the probable value of this method as an independent process for the estimation of iron, nevertheless some of the results secured would seem to warrant the conclusion that it might prove of utility as a check method, it being easy of execution and not at all time-consuming.

The following equation represents the changes which take place when the dichromate is brought in contact with the iron solution after reduction :

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

The writer has also attempted to apply the principle of the chromic acid method above described to the estimation of invert sugar, or rather to the determination of the amount of cuprous oxide thrown down from Fehling's solution in the process commonly employed for estimating reducing sugars.

The following equation represents the changes which take place when cuprous oxide is brought in contact with potassium dichromate in the presence of dilute sulphuric acid :

$$3Cu_2O + K_2Cr_2O_7 + 10H_2SO_4 = 6CuSO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 10H_2O.$$

The cuprous oxide thrown down from the sugar solution under examination is brought upon an asbestos filter connected with a filter pump and thoroughly and rapidly washed with hot water. The filter and contents are next transferred to the generating flask of the apparatus before described, and after the addition of dilute sulphuric acid, an excess of dichromate is run in.

Very thorough and long continued agitation of the contents of the flask is necessary in order to effect the complete oxidation and solution of the cuprous oxide, and the hydrogen peroxide must not be added until the solution is complete.

The oxygen liberated on the addition of the hydrogen dioxide is collected and the volume noted as before described. The equivalent amounts of chromic acid, cuprous oxide and invert sugar can be easily calculated from the data thus secured.

This method, while apparently satisfactory from a theoretical standpoint, has so far failed to give sufficiently uniform results. one of the chief objections to the process being the difficulty attendant upon the solution of the cuprous oxide.

With improvements in the details of manipulation of the process, however, it is quite possible that more satisfactory results could be obtained.

SECOND INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

BY H. W. WILEY.

Received September 15, 1896.

At the first congress held in Brussels, in 1894, it was decided to hold the meetings bi-annually and Paris was selected as the most desirable place for the reunion this year. As has already been announced to the readers of the Journal, the present congress is organized under the patronage of the French government and under the immediate direction of l'Association des Chimistes de Sucrerie et de Distillerie de France et des Colonies. The late Professor Pasteur had accepted the honorary presidency of the congress, and all delegates from foreign countries have felt an especial regret that his death has prevented them from listening to his words of welcome and from forming his personal acquaintance.

To promote the interests of the congress, committees were organized in most countries. The personnel of the one in the United States has already been published in this Journal. Through the French Foreign Office all the principal governments were invited to send delegates to the congress. Official representatives were present from Belgium, Germany, Italy, Russia, Switzerland, Austria, Portugal, Denmark, and the United States. So far as I can learn, and the fact is worthy of remark, there is no representative in attendance from England, either official or otherwise. The official delegate from the United States is Mr. C. A. Doremus, of New York, while the writer has a commission as a delegate from the Department of Agriculture, and one from the American Chemical Society, sent through the courtesy of the president and council. Belgium has the largest representation of any foreign country, and, since these gentlemen are all French in their language, the congress, as is natural, is essentially French.

The congress was formally opened July 27, at 10 A. M., in the grand amphitheater of the Sorbonne. Perhaps there is no other spot in the whole world so well suited by its history and traditions for the seat of a scientific congress, especially of chemistry. In or near the Sorbonne were made those advances in chemical science which have made famous the names of Lavoisier, Chevreul, Dumas, Deville, Wurtz, Pasteur, Berthelot, and many others scarcely less renowned. The address of welcome was fitly made by Mr. Berthelot, rendered, by the death of Pasteur, the head and front of French science. The response was pronounced by Mr. Lindet, provisional president. After these addresses, the provisional secretary of the congress presented a report showing the activity of the French and other committees and giving the number of chemists who had become members of the congress.

The congress is organized with ten sections, as follows:

1re Section.—Sucrerie.

2^{e} Section.—Industries de la fermentation: alcools, vins, bières, cidres, vinaigres.

3^{e} Section.—Industries agricoles: laiterie, fromagerie, féculerie, amidonnerie, glucoserie, matières alimentaires.

4^{e} Section.—Chimie agricole: engrais, terres, eaux résiduaires; alimentation du bétail.

5^{e} Section.—Analyses officielles et commerciales des matières soumises à l'impôt.—Appareils de précision.

6^{e} Section.—Industries chimiques: produits chimiques, pharmaceutiques; corps gras, caoutchouc, matières colorantes, papiers, tannerie, verrerie, céramique, etc.

7^{e} Section.—Photographie.

8^{e} Section.—Métallurgie, mines, explosifs, etc.

9^{e} Section.—Chimie Appliquée à la médecine, à la toxicologie, à la pharmacie, à l'hygiene et à l'alimentation. Matières alimentaires: altérations et falsifications.

10^{e} Section.—Électricité: électro-chimie.

The meetings of the congress are held in the Hôtel de la Société d'Encouragement de l'Industrie Nationale, 44 rue de Rennes, opposite the church of St. Germains des Prés and in the Hôtel des Sociétés Savantes, situated in rue Serpente, opposite rue Danton. Only four or five of the sections are in session at any one time, thus affording an opportunity to the members of the congress of attaching themselves to several sections.

In the afternoon of the first day visits were made to the Gobelin tapestries, the Museum of Natural History, botanical gardens, the National Tobacco Factory, and the Eiffel tower, the latter being reached by boats on the Seine. At the end of these visits a banquet was served on the first floor of the tower and from the tables a pleasing vision of Paris by night was obtained.

On the second day of the congress, an interesting paper was read by Mr. Moissan on the electric furnace. A large number of samples of the typical compounds obtained at the intense heat of the furnace was exhibited and a description of their physical and chemical properties given. The possibilities of the electric furnace in the near future were outlined. Mr. Moissan described in some detail the construction of the furnace. It is best made by carving a block of quicklime into the proper shape. The high infusibility of the quicklime and its non-conducting power are points in its favor. The electrodes should be of the purest carbon and there should be no deflection of the arc into the crucible. The control of the current is of the greatest importance. For instance, in the case of titanic oxide it is reduced to titanous oxide with a current of thirty ampères; at 300 ampères titanium nitride is produced and at 3,000 ampères titanium carbide. Many metallic carbides, as, for instance, calcium, yield a gas when moistened, but the gases are not identical. In addition to acetylene, hydrogen, marsh gas, and petroleum have been obtained, the latter from uranium carbide. This fact is of great interest in respect of the origin of natural gas and petroleum, which, by many, are supposed to be of organic derivation. In the furnace, molybdenum and manganese are capable of forming compounds similar to cast iron. Fine samples of chromium obtained in the furnace were shown and many specimens of various nitrides, carbides, and borides. Chromium oxide was reduced to metal before the audience and silica was sublimed.

In addition to Mr. Moissan's paper, a general discussion of electrolytic problems was held including electrolytic methods of preparing chlorine, chlorinated soda, and calcium carbide.

Mr. Moissan has accepted an invitation to attend the Princeton College celebration in the autumn and has made arrangements to give some lectures in the United States. Our chemists, therefore, will have an opportunity in the near future to hear him and to note the great progress which the electric furnace has made possible in the line of discoveries in mineral chemistry.

Another discussion of unusual interest was devoted to the official graduation of instruments of precision. It was the general consensus of opinion that a uniform 100 gram weight of platinum should be adopted by all countries, and that all instruments and utensils for weight and volume should be referred to this standard. The official meter was regarded by all to be the ultimate standard of instruments to measure length. Some of the members favored a standard of brass coated with gold or platinum, in order to have an ultimate standard of greater volume than the one made of platinum. The difficulty of securing brass of uniform and definite constitution was considered as an insuperable objection to this proposition.

Among the many papers of special interest read on this day only a few can be mentioned here by title, *viz.*, Application of Electro-Chemistry to the manufacture of Chemical Products, by M. Joly; The Difficult Digestibility of Sterilized Milk, by M. Laurent; Determination of Soil Elements Assimilable by Plants, by M. Garola; Plan and Installation of an Agricultural Experiment Station, by M. Soillard.

At 4 P. M. the sections were adjourned to visit the new city hall (Hotel de Ville), which has finally been completely restored from its destruction by the Commune. There the members were received by the mayor of the city (Prefet de la Seine), the chief of police and the chief of the fire department. After enjoying a delightful collation, such as the city of Paris knows so well how to prepare, we were conducted by the mayor throughout the building and had described to us the mural decorations and the various groups of statuary. In the opinion of experts, the new Hotel de Ville is quite equal in its artistic decorations to the magnificent structure so wantonly destroyed by the Communists in 1871.

On the third day of the congress sessions of the sections were held only in the morning. A communication was presented to the second section by Mr. Chas. J. Murphy, describing a new process of fermenting maize and showing the way to a more extended use of this product in the European distilleries. Before the third section was read several papers giving the latest European processes for the manufacture of starch. Mr. Grandeau, an agronomist well known in the United States, presented a communication to the fourth section on the assimilability of phosphates. Methods of analysis of phosphates, especially those applicable to phosphatic slags were discussed by Mr. Cluss, of Halle, and by many others. The Wagner method of solution in ammonium citrate, of a definite constitution, was advocated by nearly all those taking part in the discussion. A paper on the official German method of determining iron and alumina in phosphates, was presented by Dr. von Grueber. The method of E. Glaser, as modified by Jones, is the one which the German chemists regard as the most reliable. This method has already been described in the *Journal of Analytical and Applied Chemistry*, **5**, 671. It was pointed out that analysts had received an impression that E. Glaser had acknowledged that this method was unsound. This, however, is not the case, but the impression arose by reason of a critique of the method by C. Glaser, of Baltimore. Mr. E. Glaser died soon after publishing his method and it devolved on Dr. Grueber to continue his work. The modifications of the original method, as proposed by E. Glaser, which have been accepted by the German chemists are principally those made by Jones and with which American chemists are quite familiar. The process, as conducted by the German official chemists, is as follows:

Ten grams of the sample are dissolved in twenty-five cc. hydrochloric acid, sp. gr. 1.20, and the volume completed to a half liter. Fifty cc. of this solution, corresponding to one gram of the substance, are evaporated to half that volume in a beaker, ten cc. of sulphuric acid (one part to four of water) added and the mixture shaken. 150 cc. of absolute alcohol are added, shaken, and the beaker placed aside for three hours. The deposited calcium sulphate is separated by filtration and washed with absolute alcohol. The washing is finished when ten drops of the filtrate, diluted with the same volume of water, does not become red when a drop of a solution of methyl orange is added. The alcohol from the filtrate and washings is recovered by distillation, and the residue oxidized by bromine and hydrochloric acid, a slight excess of ammonia added and heated until the excess is expelled. This operation is very important to prevent the incorporation of magnesia in the precipitate. The residual precipitate is separated by filtration, any remaining on the walls of the beaker being washed off with cold water and a rubber-tipped tube. The whole is washed on the filter with boiling water until all traces of sulphuric acid have disappeared. The precipitate is dried, ignited and weighed and consists of the phosphates of iron and alumina. One-half of the weight of the precipitate consists of the oxide of iron and alumina.

The quantity of iron is determined by reducing the iron in fifty cc. of the first solution made, by means of zinc, and titrating the amount reduced by a solution of potassium permanganate in the usual way. The quantity of iron having thus been determined, it is calculated to oxide and subtracted from half the weight of the iron and aluminum phosphates. The difference is the alumina.

The members of the photographic section were provided with an interesting program, but the writer was not able to be present, and the total absence of any reports of the meetings in any of the daily papers, or in any other accessible form, makes it impossible to give even a summary of what was accomplished. I do not think it advisable to encumber the pages of the Journal with a complete list of the papers presented, inasmuch as the presenting of the titles of the papers would fill many pages and give but little idea of the proceedings. Moreover the published program, although extensive, does not include perhaps more than half the titles of the papers presented, and I am not sufficiently acquainted with the French way of doing things to be able to complete the list. Only one program of papers and proceedings has been printed, and that evidently is to serve for the whole congress. The French in this particular might well imitate the practice of the American Association for the Advancement of Science in providing daily programs.

Interesting communications were presented to the ninth section on food adulteration, and Mr. Doremus read a paper on the nature of the gases contained in canned goods. He showed that these gases were chiefly hydrogen and probably the hydrogen is produced by galvano-electric action in the metals of the can. In all cases where much gas was found, the sides of the can were found deeply corroded. There was no evidence in these cases of the action of ferments and in every case the sterilization of the canned goods was perfect. Mr. Thomas Taylor sent to the section a communication on the crystals of butter fat embodying the results of his observations while chief of the Division of Microscopy of the Department of Agriculture. Mr. F. Jean read a communication on the distinction between butter and margarine as determined by his instrument, the oleorefractometer. This instrument has been carefully tested in the Chemical Division of the Department of Agriculture, and while it has been found to give valuable indications it is by no means so definitely diagnostic as its inventor claims.

Before the eighth section were presented memoirs on the methods of determining sulphur, phosphorus, nickel and carbon.

The afternoon of the third day (Wednesday) was given over to a visit to the celebrated agricultural school and experiment station at Grignon. The members of the congress traveled by railway to Versailles where carriages were provided to conduct us to Grignon. Passing the palace and garden of Versailles, we entered the forest and after two miles reached a stretch of fields which for beauty and fertility are scarcely equaled in the world. The wheat and oats harvests were going on and I was impressed with the primitive methods employed. The cradle and the sickle are almost universally used, only one reaping machine being seen in a drive of ten miles. At Grignon the tourists were received by Mr. Philippar, the principal of the school, and by Mr. Deherain, the director of the station, whose name and fame are well known to all chemists, especially those engaged in agriculture in the United States.

The experimental plots of the station were explained by Mr. Deherain, and thereafter, in his laboratory, he gave a brief explanation of the charts representing the results of the experiments for many years. After leaving the experiment station, the members of the congress were driven over the farm connected with the school and they also inspected the barns, stables, horses and herds of sheep and cows. I noticed that much of the agricultural machinery, especially the reapers, hay-rakes and plows, were of American manufacture. The college buildings are part of an old chateau which, under the first empire, belonged to one of the marshals of France. The school at Grignon is the largest and most important of the three national colleges of agriculture. The other two are established at Montpellier and Rennes respectively. Three classes of pupils are admitted; *viz.*, internes, who pay $240 a year, demi-internes, who pay $120, and externes, who pay $80. Others known as free auditors are also admitted to all the lectures and pay $40 a year. The course of instruction lasts two years and a half and includes zoology, botany, mineralogy, agricultural geology, physics, meteorology, general and agricultural chemistry, agriculture, horticulture, arboriculture, viticulture, sylviculture, rural economy, entomology, sericulture, apiculture, technology, agricultural legislation, hygiene and military exercises. The number of pupils admitted to each class is fixed annually by ministerial decree, and is limited also in the class of internes by the number of beds. The total number of pupils, excluding the free auditors, is about 250. On the completion of the course and passing a satisfactory examination, which shall merit at least sixty-five out of a possible 100 points, the pupil receives the diploma of the National School of Agriculture, and four-fifths of the whole number thus graduating, comprising those who have received the highest marks, are excused in time of peace from all military service, except one year.

Examinations for admission to the school are competitive and include arithmetic, algebra, geometry, trigonometry, elementary physics, chemistry, zoology, botany and geology. The chemical instruction is given by Mr. Deherain and his assistants and consists of lectures and demonstrations in general and agricultural chemistry, including the chemical study of plants, soils and fertilizers. It is evident, however, that in the short time at their disposal the students can not acquire great efficiency in chemical manipulations and in fact it is not the object of the school to train agricultural chemists, but rather to provide young men with that character of instruction which will enable them to manage with intelligence and in harmony with the most advanced teachings of science, large landed estates.

Those members of the congress who did not desire to visit Grignon were offered an alternative excursion to the nickel works of Messrs. Christofle, Bouilhet and Cie., at Saint Denis. I have not been able to secure any reports of this visit.

The fourth day of the congress, July 30, was devoted exclusively to the honor of the late M. Pasteur. At 9.30 in the morning, the members assembled in the chapel of Notre Dame and placed a memorial wreath on Pasteur's coffin. The body of the illustrious savant lies in an alcove near the middle of the north side of Notre Dame, the coffin scarcely visible beneath a mountain of wreaths and crowns. Not only is the alcove in which the coffin rests full of these offerings, but they have been stored, in cart-loads, in all the adjoining alcoves. They come from individuals and learned societies from all parts of the world and from nearly every municipality in France. The coffin rests here temporarily until the tomb and monument, to be erected by popular subscription from all parts of the world, are ready. The final resting place of the body of Pasteur is to be in the court of the Pasteur Institute. With bowed heads the members of the congress marched by the coffin holding only the motionless brain whose activity has done so much to advance knowledge and benefit mankind. Thence the carriages conveyed us to the Pasteur Institute where the laboratories were inspected. A collection of many compounds of historical interest, prepared by Pasteur, was on exhibition, among which were all the tartaric acids and tartrates used by Pasteur in demonstrating molecular asymmetry as displayed by the same chemical substance having opposite relations to polarized light. A large collection of original cultures of the ferments leading to the discovery of antidotes for rabies was also on exhibition. A large number of microscopes showing the specific microbes of phthisis, cancer and diphtheria attracted general interest. In the clinical rooms we were permitted to see one of the daily inoculations with antirabic serum. About thirty patients were treated in less than half that number of minutes. About two or three cc. of serum are administered by hypodermic injection to each patient. The serum is inserted in the skin on the right or left side of the abdomen, the most convenient place on account of the infrequency of nerves. Each patient receives from ten to fifteen injections on successive days. About 150 patients are received monthly, and the treatment is entirely gratuitous. Those who are able, however, usually give generously to the funds of the institute. A large collection of rabbits, guinea pigs and dogs, serving for experimental purposes, was also inspected. We were next driven to St. Cloud and through its beautiful gardens and forests to Garches, where a delightful breakfast was served at one o'clock. After breakfast a visit was made to the stables containing the horses used to furnish the anti-diphtheritic serum. There are 120 of these and all seemed to be in perfect health. Each one of these horses has been inoculated with the diphtheritic poison and the blood thereafter serves as the source of the serum. Two horses were operated on as an illustration of the method of work. A large vein in the neck of the animal is opened, a tube inserted and the blood collected in a sterilized jar. So skillfully is this accomplished that scarcely a drop of blood is lost. From four to six liters of blood are collected from each animal, when the vein is closed and the horse returned to his stall. In three or four weeks he is ready to supply another quantity of blood. The jars containing the blood are placed in a cupboard for about forty-eight hours, when, if the horse has been properly inoculated, their contents will be found sharply separated into clots and serum. The serum, which is of a light yellow color, is removed by decantation and by an ingenious apparatus, which prevents all danger of infection, is bottled in vials containing ten cc. each. One horse was shown us that had furnished in the past few years several hundred liters of serum. He appeared to be good for many hundred more. The serum thus prepared is used directly by subcutaneous injection on patients suffering from diphtheria. Every appointment in these stables was such as to impress the visitors with a new and a noble idea of science, ministering thus directly to saving life and especially the lives of children. No wonder the body of him who did so much to establish the lines of investigations which, under his immediate direction, if not by his own hands, have led to such ameliorations in the sufferings of men, lies to-day in honor in one of the most magnificent churches in the world, buried under flowers and wreaths, while the memory of his work lives immortal in the hearts of the people it has blessed.

Next was inspected the national porcelain works at Sèvres, reached after a pleasant drive from Garches. The officials of the factory received the guests at the entrance and dividing the visitors into small parties each was personally conducted through the works. Beginning with the crude materials, kaolin, quartz, etc., the methods of grinding and mixing were first explained. The character of the mixing is of course suited to the nature of the object in view, the massive urns and vases having a different proportion of the several ingredients from the delicate cups and saucers. The molding of the objects was shown in detail in its three forms; *viz.*, by carving the solid moist mass, by allowing it in a pasty state to flow into moulds, and by turning the waxy mass on a table and imparting the desired form by the hands of the operator. The urns and vases are made by the first and third methods, while the thinner vessels, such as cups, etc., are made by the second method. After drying, the glaze is applied by dipping the objects in a creamy bath of the silicates serving to form the glaze. After the glazing is fixed by firing, the objects are passed to the decorating room to receive their final colorings. After each color is applied, it is fixed by firing. The ingenious hoods used to secure an even firing of the objects were exhibited and the manner of using them shown. The construction of the large furnaces where hundreds of vases and other objects are fired at once, was described, and the furnaces cold and in action exhibited. The visit concluded with an inspection of the museum and salesrooms with their artistic and costly contents. These are known to all visitors, but the process of manufacture which was so minutely shown us is not open to the public in general. The day was finished by a drive back to Paris through the parks of Meudon and Boulogne.

Having taken the whole of the fourth day for the interesting and instructive excursions which have just been briefly described, the fifth day, Friday, July 31, was wholly devoted to the scientific work of the congress. Sections 1, 2, 4, 5, 9, and 10 held morning sessions, and 2, 3, 5, 6, 8, and 9 met in the afternoon. The time of Section 1 was devoted to a discussion of the crystallization of sugars and the methods of suppressing the molasses in the manufacture of sugar from canes and beets. The papers presented and the discussions thereon were more technical than chemical.

In the second section, the difficulties attending the detection and estimation of the higher alcohols, aldehydes and ethers in brandies and whiskies were set forth and Mr. Tavildaroff, of St. Petersburg, gave a résumé of the best methods of procedure.

In the third section the methods of determining phosphoric acid in soils and fertilizers were again the subject of discussion and papers on this subject were presented by Messrs. Garola and Sidersky. Mr. Lasne presented a résumé of his work on the detection and estimation of iron and alumina in phosphates. In section 5, papers on the analysis of fats, estimation of acetic acid in pyroligneous acid, a new method of estimating alcohol by means of the ebullioscope, and a rapid method of analyzing denaturalized alcohol were presented by Messrs. Jean, Kestner, Wiley, and Guillier, respectively.

In the ninth section, the application of the spectroscope in medico-legal cases was discussed. In connection with a discussion of the influence exerted by ptomaines on the detection of alkaloids in medico-legal cases, Mr. Dorenlus presented a paper entitled "Recovery of Morphine from a Cadaver Embalmed with Arsenical Solution."

The subject of the possible detection of toxines in potable waters was also discussed and the influence exerted on them by organic matters in process of decomposition pointed out.

In the afternoon, in section 2, a paper was presented by Mr. Kayser on the properties of yeasts of different origin. A subject of interest to the wine growers of our southern states and California was a paper on the vinification in warm climates, by Mr. Dugast. The pasteurization of wines was discussed in a paper by Mr. Malvezin. Other papers of interest to wine makers were presented and discussed.

To chemists and bacteriologists engaged in the manufacture and study of butter and cheese, the proceedings in section 3 were of great interest. The best methods of disinfecting stables and creameries by chemical means were presented by Mr. Bordas. A résumé of our knowledge concerning the influence of food on the composition and character of milk and butter was presented by Mr. Martin. A general discussion of the best means of providing cities with pure milk was led by Mr. Saillard. The importance of selecting ferments in the manufacture of butter and cheese was discussed by the section, but the work done by Conn and others in the United States did not seem to be appreciated.

In section 3 a paper on the effect of impurities on the properties of metals was presented by Mr. Le Verrier, and the methods of micrographic and photomicrographic examination of metals and alloys were described by Mr. Osmond.

In section 5, Mr. Jobin presented a paper giving the data for comparing the different saccharimetric scales in use in the determination of sugar by the polariscope, and the method of securing a uniform scale was discussed by Mr. Sidersky. It was voted that a quartz plate of exactly one millimeter thickness was the most scientific standard by which to measure or fix a saccharimetric scale. The most probable value of this standard at the present time is expressed by an angular rotation of 21° 40′.

In section 8, papers were read by Mr. Lasne on the phosphate industry, by Mr. Th. Schloesing on the condensation of vapors at a high temperature, on the ammonia industry by Mr. Truchot, and several other papers of less importance.

In section 9, the subject of the analysis of urine and the determination of urea was discussed by Messrs. Monfet, Taffe, Hodencq, Vicario, Hugnei, Barthe, Girard, and Doremus, the latter describing an apparatus for the purpose, invented some time ago by himself, and also the use of bromine dissolved in sodium bromide, as proposed by Rice.

In the evening a lecture was given to the congress in the amphitheatre of the Sorbonne on color photography by Mr.

Lippmann, who has achieved an international reputation by his researches into this important process. The principles of color photography were described and illustrated by apt experiments in conjunction with a projecting lantern. The process developed by Lippmann is based on the well known properties of thin films, as, for instance, a soap bubble to show colored bands due to the relation between the thickness of the film and the length of the waves of light. Mr. Lippmann has succeeded in depositing on a glass plate superimposed films of silver of extreme tenuousness and each of these films differs in thickness for each variation of color in the object producing the photograph. When the photograph is thus constructed it happens that when it is viewed by reflected light, every color of the object photographed is exactly reproduced. A large number of these photographs, representing paintings, flowers, landscapes and persons, was projected by reflection with the most vivid verisimilitude. Perhaps the most interesting of these was the spectrum of argon, in which the blue bands were shown in perfectly natural colors and clearly defined. The photographic effect is secured by exposing a perfectly transparent sensitive plate, backed by metallic mercury, in contact with the film. The sensitive surface of the plate is turned away from the object to be photographed. The plate holder for this operation was shown and is remarkable alike for its ingenuity and simplicity. The importance of color photography, as a means of fixing objects for study, is as great as its usefulness will prove to be in preserving with all the tints of vitality the faces of friends and the beguilements of beauty.

Mr. Lippmann kindly granted to Mr. Doremus and myself a private interview after the lecture, where we had a better opportunity to examine the negatives. They resemble the daguerreotypes of forty years ago and a distinct view of the image is only obtained by inclining the plate in the proper manner to secure the reflection of the light. Unfortunately, these negatives are not capable of being reproduced as positives as in the case of ordinary photography, and we are apparently as far away as ever from multiple printing color photography.

Sixth day, Saturday, August 1. Sessions of the sections were held only in the morning and those meeting were 1, 2, 4, 6, 7, 8 and 10.

In the fourth section Mr. Kjeldahl gave a brief statement of the present methods of conducting his process for the determination of nitrogen by moist combustion. Papers on methods of detecting and preventing frauds in the sale of commercial fertilizers were presented by Mr. Petermann. A paper on the importance of international agreement in methods of agricultural analysis was presented by the writer. A general discussion of official methods of analyzing fertilizers was carried on, and at the end it was voted that the congress collect and publish in German and French the official methods of France, Germany and the United States. Mr. Sidersky was selected as editor of this brochure.

Messrs. Roy and Jean gave a paper in section 6 on tannins, their nature and analysis. It contained little that is new to American chemists and showed a lack of familiarity with the American publications on that subject.

In section 7 Mr. Vogel presented a paper on photography in colors, and one on the same subject was presented by Mr. Vidal. These papers gave in detail the points given *en résumé* in Mr. Lippmann's lecture.

In section 9, Mr. Guichard read a paper on alcohol from a hygienic point of view.

The employment of aluminum in the construction of cooking utensils and its influence on the wholesomeness of food prepared therein was the subject of a paper by Mr. Boroma. It was shown that with proper precautions aluminum could be safely used, but that it presented few if any advantages over copper or other metals in common use.

So widely has aluminum come into use for cooking utensils that a brief abstract of our present knowledge concerning its merits may be presented. The utility of an aluminum dish, in respect to its fitness for culinary vessels, depends on the purity of the metal. A pure aluminum dish is almost if not quite as resistant to solvent effects of ordinary foods as any common metal. The impurities which do the most harm are sodium and carbon. When the aluminum contains carbon an electric current is at once set up when a suitable liquid is applied. In such cases after water, especially if it be saline, has stood in the dish for one or two weeks, the surface will be found dotted with brilliant rings, and on scraping off the aluminum the particle of carbon will be disclosed. If a strong solution of salt be used, the action may be sufficient to cause a perforation of the metal. The aluminum of commerce, unfortunately, is not very pure, and it is for this reason that so many aluminum dishes have shown a rapid deterioration. The French troops in Madagascar have been supplied with 15,000 sets of aluminum dishes, and, when a soldier has to carry his kitchen with him, the importance of lightness is not to be despised. But even granting that in cooking in aluminum dishes a small amount of alumina is introduced into the food, it has not been shown that it exercises the least harmful action on the digestion. The experience of two men may be cited who lived for a year on food prepared exclusively in aluminum dishes without the slightest impairment of their health.

In the afternoon the members were driven in carriages to Gennevilliers, where they inspected the irrigation works, lately constructed to supplement those at Asniéres in disposing of the sewage of Paris. It has now been more than a quarter of a century since the city of Paris has been using its sewage for irrigation. The fact that in the light of that long experiment it has recently more than doubled the area under irrigation, shows that the process is considered a practical success. The sewage of Paris consists mostly of the water used for washing the streets. Water-closets are, to a large extent, connected with vaults whose contents are removed by means of wagons, pumps and closed tanks during the night. The sewage, therefore, is not so highly polluted nor so rich in fertilizing materials as might have been supposed. For summers like the present one, which has been excessively dry, the disposal of the sewage by irrigation is easily accomplished. But in summers of excessive rainfall and in the winter, the problem is much more complex.

We first were shown a plan on a large chart of the system of sewers and the distribution of the waters. Next the pumping house was visited where the sewage is raised to a sufficient height to carry it under the Seine by a siphon aqueduct and distributed to the irrigated fields. The fields which were inspected are only a part of the vast system of irrigation now in operation. They contain 799 hectares, a part of which was once covered by the old forest of St. Germain. The city of Paris spent 200,000,000 francs in the purchase of the grounds, the building of the aqueduct, erecting the pumping machinery and building the irrigating canals. The work on the aqueduct of Achéres was commenced in 1893 and the whole work was completed in 1895. The aqueduct is eleven kilometers long and is three meters interior diameter, and it crosses the Seine, which below Paris forms a loop, twice. Fortunately, the soil, forming the basin of the Seine in this locality, is of a sandy nature and permits a somewhat rapid filtration. A clay subsoil would render the whole process inapplicable. The gardens, though only two years old, presented a scene of almost tropical exuberance. Many dwarf fruit trees were already in bearing and older trees showed the existence of orchards before the present system was inaugurated.

The methods of irrigation are exactly those practiced in the arid regions of the United States. The water is conducted in furrows on the surface between the rows of growing crops. Aside from a slightly unpleasant odor arising from the sewage, there is nothing in the scene to cause the observer to look on the perfect vegetables and flowers with suspicion. In harmony with the French devotion to art, the borders of all the plots are planted in roses and other flowers and these, at the time of our visit, were all in full bloom, recalling in their floral exuberance the gardens of California. Here, as a result of the applications of science, typhoid fever is turned into turnips, dysentery dances in the dew on the dahlias, and cholera comes chortling as cabbage. The one unpleasant reflection is found in the fact that this extensive harvest is sold exclusively in the Paris markets and one can hardly avoid thinking in the restaurants over his cauliflower and artichoke of the long race they may have run in the aqueduct of Achêres. At the end of the experimental field, next to the river, the sewage which has passed through the soil reappears as a large stream of pure water, absolutely colorless and bright. Glasses of the attractive fluid were offered the visitors, many of whom, unmindful of miasm and microbes, drank, willing martyrs to science or curiosity. The number of micro-organisms, which is many millions in the sewage, is diminished to 2,500 in each cubic centimeter of the filtered water.

Seventh day, Sunday, August 2. An excursion was offered to the members of the congress on Sunday to Compêigne. On reaching the station, a band of music welcomed the excursionists. They were driven through the gardens and forests in carriages and at one o'clock a breakfast was served.

Eighth day, Monday, August 3. In section 1 papers were presented on the methods of determining water in organic viscous liquids, by Mr. Pellet. The process recommended is by absorption with pumice stone and subsequent drying, first at 60° to 80° and finally at 100°. Molasses and solids should first be dissolved in water to promote absorption by the pumice. A drying dish was exhibited with a circular depression in the center, into which the body is weighed and mixed with enough water to make it flow easily. The fragments of pumice are placed on the flat bottom of the dish, exterior to the depression, and the dissolved mass is absorbed by the pumice on inclining the dish. The dish and cover are made of aluminum. The diameter of the dish is about seven and its depth two cm. The composition of molasses derived from the sugar cane was discussed at some length. Raffinose, to the extent of three per cent., has been detected in samples of cane molasses of Egyptian origin. The reducing sugar, in cane molasses, according to the statement of Pêllet, is composed solely of invert sugar, a conclusion which he has reached by applying the method of estimating levulose described by the writer in this Journal a few months ago.[1]

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[1] Vol. 18, No. 1, p. 81.

An interesting paper by Mr. Herzfeld, of Berlin, gave a résumé of the best methods of separating sugars in mixtures.

In section 3, the session was devoted to the chemical study of processes of bread making, and especially to the methods of analysis of moist and dry gluten. The processes presented are almost identical with those in use in the United States. Mr. Lindet, the president of the congress, read a communication on the methods of determining starch in grains and flours, in which the separation by a ferment or by water under steam pressure was recommended as the best. These are the processes which we have preferred for several years in the agricultural laboratory at Washington.

In section 6, papers were presented on gutta percha, paper, and paint used to prevent corrosion of ship bottoms.

In section 9 a paper on the analysis of wines and vinegar was presented by Mr. Leroy. The detection of glucose in beer was discussed by Mr. Padé. The question of fermentation and the germicidal methods of controlling it by means of fluorides was discussed by Mr. Effront.

An interesting exhibition was given of the workings of the latest form of bomb calorimeter for the determination of the thermal equivalents of foods.

Among the more interesting papers presented in the afternoon may be mentioned one by Mr. Fernback, director of the laboratories of the Pasteur Institute, on the utilization of the carbon dioxide arising from fermentation, in section 2; the influence of culture on the chemical and physical properties of the soil, by Mr. Deherain, in section 4, and the estimation of lactose and sucrose in condensed milks, by Mr. F. Dupont, the general secretary of the congress, in section 5.

In the evening a banquet was given to the chairmen of committees of organization and to the delegates of foreign governments, in the Salle des grandes Fêtes of the Grand Hotel, under the presidency of Mr. Cochery, Minister of Finance, at which nearly 500 sat down. An orchestra rendered beautiful music during the repast, giving among other things the national airs of the various governments represented. "Yankee Doodle" doubtless was heard with equanimity, but one can imagine the feelings of the Frenchmen present when "Die Wacht am Rhein" was given. Short addresses were made by Mr. Lindet, the president of the congress, by Mr. Doremus, on the part of the foreign delegates, and a rather long one by the Minister, who greeted the chemists for many reasons, and especially, he said, "because you are the precious auxiliaries of my department in promoting the production of articles that can be taxed." Mr. Doremus introduced his address by quoting one of the inscriptions on the statue of Danton : " Apres le pain l'education est le plus grand besoin du peuple." He alluded to the addresses of Berthelot, Moissan, and Lippmann, as illustrations of a few of the accomplishments of applied chemistry, and said the congress had shown in a striking manner the necessity of a close alliance between applied and research science. Pasteur will owe his immortality to the great faculty he possessed of finding a practical application for his discoveries. He concluded as follows : " Hon. Minister of Finance, representing the French Republic, M. Berthelot, the illustrious president of honor of this congress, M. Lindet, the president of the congress, M. Dupont, the secretary, I wish to thank you in behalf of the foreign delegates, for the hospitality, friendship, and good fellowship with which we have been received. In the name of the foreign delegates, I propose this toast, the French Republic, patron not only of this congress, but also of science, art and industry, the mother of men famous in each science, but especially, in chemistry."

The strangers present were given a very favorable opportunity to understand the heartiness of French hospitality and the excellence of French cooking. We might learn more things than good cooking from a French banquet and among others the art of limiting the post prandial speeches. At ten o'clock the guests left the table and assembled in the grand salon, where coffee and liqueurs were served and an hour or more spent in social intercourse.

Ninth day, Tuesday, August 4. I have already used so much space in giving even a few of the details of the congress that it is not advisable to mention even the more important communications presented to-day. Morning sessions only were held. In the afternoon the Conservatoire des Arts et Métiers was visited, where the congress was received by Mr. Aimé Girard, the professor of applied chemistry, and shown through the laboratories and museums. In the latter alone are enough objects of interest to employ the time of a scientist for a month for a careful study. We can only mention *fastigia rerum*. The pendulum used by Foucault in his classical experiments is still swinging and showing by its deflections the rotation of the earth. All the important apparatus used by Lavoisier is collected here. The globes employed by him for determining the composition of water are remarkably well made and even to-day would be regarded as entirely convenient. But they have their chief value as the remains of those era-making investigations, cut short by the guillotine, which laid the foundation of modern chemistry. A wooden wheel, preserved by the copper sulphate in an abandoned copper mine since the fifth century, illustrates in a most striking way one of the best methods of preventing decay in railroad ties. The standard measures of all nations make an interesting collection, but, unfortunately, we were not permitted to see the original meter, which is preserved from view in the vaults of the building. In the courtyards are bronze statues of Le Blanc, who made the fortunes of so many and committed suicide by reason of his own poverty, and of Boussingault, the contemporary of Liebig and the father of French agricultural chemistry. A photographic view of the congress was made on the steps of the west façade of the building.

Tenth day, Wednesday, August 5. In the morning the sections held their final sessions for hearing papers and discussions. In the afternoon the closing meeting of the congress was held in the grand amphitheatre of the Sorbonne under the presidency of Mr. Henri Boucher, Minister of Commerce and Industry. Addresses were made by Mr. Lindet and the Minister and a report of the proceedings of the congress presented by the secretary, Mr. Dupont. Turin and Vienna were placed in nomination as the places of meeting of the congress in 1898. Vienna was selected by a large majority. An invitation was extended by Mr. Lindet to hold the congress of 1900 in Paris during the World's Exhibition, and that invitation will doubtless be accepted at Vienna.

After the adjournment of the meeting, the new laboratories of organic chemistry, constructed by Friedel, were inspected by Mr. Doremus and myself. In the confusion of the summer cleaning, we could hardly form any favorable judgment of their points of excellence. The ultra impressionist painting of Paradise Lost, a mural ornamentation back of the professor's lecture table, was the most original and inexplicable feature of the laboratory.

PARIS, August 10, 1896.

NOTE.

The fourteenth annual report of the Committee on Indexing Chemical Literature was presented to the American Association for the Advancement of Science at the Buffalo meeting, August 24. A large amount of work has been done in this field during the year. The committee is an active one and has done a valuable work in encouraging and recording biographical undertakings. Copies of the report may be obtained of the chairman, Dr. H. Carrington Bolton, Cosmos Club, Washington, D. C.

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A NEW FORM OF POTASH BULB.[1]

BY M. GOMBERG.

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THE potash bulb most frequently used at present in elementary organic analysis is that known as Geissler's bulb. While neat and compact, it still has the same drawback as possessed by other forms of potash bulbs; namely, that even with the most careful handling it is not unfrequently broken. Some two years ago I drew up a design for a different form of bulb, wherein all the connections should be enclosed. Several attempts to have it made in this country have proven unsuccessful. The design was then sent to Greiner & Friedrichs, of Thüringen, and I have recently received from them samples of such bulbs. Meanwhile, it came to my notice that a bulb based on similar principles has been put upon the market by Bender & Hobein, of München. A comparison of the two bulbs shows them, however, to be sufficiently different to justify me in presenting a description of the one made according to my design, without claiming priority as to the principle of construction.

The arrangement and working of the bulb will appear clear from the subjoined diagram, which presents the apparatus reduced to one-half its actual size.

The potash bulb is divided into three compartments, *A*, *B* and *C*. *B* and *C* contain the potash solution for the absorption of the carbon dioxide, while *A* serves as a safety reservoir in case of backward suction. The bulb is filled by dipping *a* into the solution, and applying suction at *b*, until the two com-

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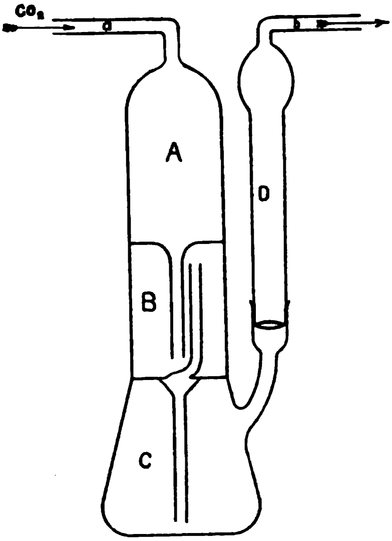
[1] Communicated by A. B. Prescott. Read at the meeting of the American Chemical Society, Buffalo, N. Y., August 22, 1896.



partments *B* and *C* contain as much of the solution as would completely fill *A*, which is about thirty-five to forty grams of a 2 : 3 solution. *D*, which is fastened to the bulb by means of a ground-glass joint, contains solid potassium hydroxide, or soda-lime, supported by a plug of glass-wool. The liquids in *B* and *C* can be easily mixed when desired, by applying suction at *a*. The bulb, when filled and ready for use, weighs from sixty-five to seventy grams, and undoubtedly can be made even much lighter.

The total number of compartments is thus reduced from five in Geissler's form to three in the form here presented, while the absorbing chambers are reduced only from three to two. The construction of the bulb is such that *C* can never get overfilled by the solution from *B*.

This form of a potash bulb possesses the advantages first, that it can be easily handled and wiped, presenting the outside surface of an ordinary small flask, and second, that it can be set without any support, and can be weighed without suspending it if so desired.

I wish to express my thanks to the firm of Greiner & Friedrichs, of Thüringen, who have kindly made the bulb for me in a most satisfactory manner.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.

REDUCTION OF CONCENTRATED SULPHURIC ACID BY COPPER.

BY CHARLES BASKERVILLE.

Received August 27, 1896.

IN a previous communication[1] the writer noted that copper was acted upon by concentrated sulphuric acid (1.84 sp. gr.) not

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[1] This Journal, 17, 90.

only at the ordinary temperatures of the air, 20°-30° C., but at zero as well. Andrews[1] states that the assertion is incorrect and that it does not occur until the temperature 86° C. has been reached, or a point above the dissociation temperature of the concentrated sulphuric acid, 67° C., according to him. Andrews further says that the author's statements were based "not upon any demonstrations of the formation of sulphurous acid, but solely on the formation of copper sulphate," which, he says, occurs only "in consequence of the presence of the air." It is to be regretted that Dr. Andrews did not note carefully the statements of the author in his previous communication, as no reason whatever exists for any such conclusions, because it was distinctly stated that not only the copper as sulphate, but as sulphide was determined, as well as sulphurous acid, and moreover, that the experiments were carried out when the air had been replaced by a neutral gas, either hydrogen or carbon dioxide.

The author, although confident of the correctness of his former statement, carried out further experiments to correct the error, if committed or to establish, beyond question, the fact that concentrated sulphuric acid of 1.84 sp. gr. is reduced by copper below 86° C., the limit *positively* set by Dr. Andrews.

The fact that these experiments but confirmed the former statement of the author allows the incorporation of the results in this paper.

As far back as 1834 the fact that copper is acted upon by concentrated sulphuric acid at ordinary temperatures, if sufficient time be given, was made known by Barruel.[2] Calvert and Johnson,[3] however, failed to obtain any action below 130° C. and considered that none took place. Pickering,[4] however, stated that "sulphuric acid attacks copper at all temperatures from 19° C., (and probably even still lower) upwards."

First Experiment.—Copper ribbon in strips, 1 x 3-4 cm., was submerged in concentrated sulphuric acid in a clean glass stoppered flask for a month. At the end of that time not only were there white crystals of anhydrous copper sulphate clinging to

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[1] This Journal, 18, 253.

[2] *J. de pharm.*, 20, 13, *1834*.

[3] *J. Chem. Soc.*, 19, 438, *1866*.

[4] *J. Chem. Soc.*, Trans., *1878*, 113.

the sides of the containing vessel, but there was a very appreciable amount of brownish black cuprous sulphide and sulphur dioxide was easily detected by its strong odor when the vessel was opened.

Andrews[1] states "that in the presence of air sulphuric acid is attacked by copper at ordinary temperatures, but without reduction of the acid. The reaction must take place according to the equation,

$$2Cu + O_2 + 2H_2SO_4 = 2CuSO_4 + 2H_2O."$$

Formerly the author[2] stated that the presence of the oxygen of the air when it comes into contact with the copper in the acid has great influence on the reaction. Fifty years ago, Maumené[3] proved that when a current of oxygen gas was passed through the boiling acid, the amount of insoluble residue, *e. g.*, cuprous sulphide, was diminished, that is, less than there would be formed if the experiment were carried out with a current of carbon dioxide. The copper must be directly exposed to the oxygen by only partial submersion or the bubbling of the air against or around the submerged copper; but the air in a confined space, not at all in contact with the copper, but separated by a thick layer of concentrated sulphuric acid, has little or no effect.

Yet grant that the oxygen of the air (volume of air about 200 cc.) confined in the flask, had been utilized in the formation of the copper sulphate produced. According to the formula given above, the oxygen would be absorbed and no corresponding amount of any other gas would be eliminated; consequently there should be a greater external pressure at the close than at the beginning of the experiment. When the smoothly fitting glass stopper was removed, not only no extra internal pressure was noticed, but in fact a pressure from within. This was evidently produced by the sulphur dioxide generated. The sulphur dioxide was swept out by a current of air through a dilute solution of potassium permanganate, which was quickly bleached. The presence of sulphur dioxide was further proven by the addition of barium chloride to the bleached potassium permanganate

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[1] This Journal, 18, 252.

[2] *Ibid*, 17, 912.

[3] *Ann. chim. phys.*, *1846*, [3], 18, 311.

solution. Nor does the formula given above account for the cuprous sulphide which is always produced.

Second Experiment.—Realizing the possibility of some organic matter or dust remaining in the flask, although it had been carefully cleansed, the first experiment was repeated with the greatest precaution to ensure the absence of dust. The flask was scoured with boiling concentrated pure sulphuric acid containing potassium bichromate and carefully cleansed with distilled water. The last traces of water were removed by four subsequent washings with the same kind of concentrated acid used throughout the experiments. The experiment was carried out in the same manner as the first, the same results being obtained.

A blank experiment was carried out at the same time. The flask was rendered dust free in the manner just mentioned and fifty cc. of the same acid allowed to remain in the flask for six months. At the end of that period not a trace of sulphur dioxide could be detected in the blank, therefore the sulphur dioxide produced when the copper was inserted could not be due to the reduction of the sulphuric acid by an extraneous substance, but solely by the copper. The conclusion is that sulphuric acid is reduced by copper when air is present at the ordinary temperatures, 20°–30° C.

Third Experiment.—An ordinary Kjeldahl digestion flask was made dust free by the treatment noted above. 100 cc. sulphuric acid, 1.84 sp. gr., were placed therein and clean dry strips of copper ribbon were completely submerged in the acid. Now air-free carbon dioxide was passed through the flask for three hours. The inlet tube was just dipped into the acid. The flask was then attached to a suction pump, with a sulphuric acid drying flask intervening to prevent a possible return flow of gas or air which might carry moisture or dust into the flask. The flask was exhausted of the carbon dioxide present for three hours at a pressure of 150 mm. It was then sealed with the blast lamp and placed aside in a darkened cupboard. Observations were made every few days to note any reaction taking place. Within two days it could be easily seen that copper sulphate had been formed and the liquid was somewhat clouded by very finely divided suspended cuprous sulphide. Continued observations extending over a period of seven weeks showed only an increase in the amounts of both of these substances. The temperature of the cupboard had at no time risen above 20° C., and was for most of the time much lower. The flask was then opened as any other sealed tube, and instead of an external pressure inward, which had been sufficient to heavily dent the tube in sealing, there was a strong internal pressure outward. The gas evolved was sulphur dioxide, easily detected by its strong odor and bleaching effect upon a dilute solution of potassium permanganate. The sulphuric acid produced by the oxidation of the sulphur dioxide by the permanganate was precipitated by barium chloride. All solutions and apparatus were proven to be free from traces of sulphur dioxide and sulphuric acid by a blank experiment.

Conclusion.—Concentrated sulphuric acid, 1.84 sp. gr., is reduced by copper when air is absent and at temperatures far below 86° C., in fact at the ordinary atmospheric temperatures with the formation of copper sulphate and cuprous sulphide and the production of sulphur dioxide.

Finally.—Apparatus similar to that made use of by Andrews[1] was employed with the modification of having three drying flasks containing concentrated sulphuric acid instead of one, and a Meyer absorption tube was substituted for a single small flask. These served merely as extra precautions against dust and insured an intimate mixing of the outgoing gases with the permanganate. Within twelve hours the permanganate was bleached. Andrews' experiment lasted only fifteen minutes. The presence of the sulphur dioxide produced was easily detected by the odor when the apparatus was opened, and in the bleached permanganate solution by barium chloride. Copper sulphate and cuprous sulphide were also formed.

Concentrated Sulphuric Acid is Acted upon by Copper at Zero.—Quantitative experiments were carried out by the author when the concentrated sulphuric acid in which the copper was submerged was practically at zero.[2] In stating the results, however, the author gave the temperature as "0°–10° C." The flask

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[1] This Journal. 18, 251.

[2] *Ibid.* 17, 908.

containing the acid was buried in an ice-bath and the temperature of the liquid noted by a thermometer inserted through a rubber stopper. The apparatus was air-tight. A stream of hydrogen gas was continued through the apparatus in one experiment for six weeks and in another two months. On two occasions when the ice in the bath had melted in going over Sunday, the temperature rose to 10° C. The temperature could not possibly have remained that high for over twelve hours, which would have had small influence when the experiments lasted through a number of days. The temperature was reported 0°–10° C., however. Not only copper sulphate, but cuprous sulphide and sulphur dioxide had also formed. Copper, therefore, decomposes concentrated sulphuric acid (sp. gr. 1.84) practically at zero.

From my own experiments and from experiments performed with apparatus similar to that used by Andrews and under the same conditions, except with regard to the important element, time, which consideration is necessary for all chemical reactions, the author must adhere to his former statement.

UNIVERSITY OF NORTH CAROLINA.

THE SEPARATION OF THORIUM FROM THE OTHER RARE EARTHS BY MEANS OF POTASSIUM TRINITRIDE.

BY L. M. DENNIS.

Received September 4, 1896.

SOME time ago the author and F. L. Kortright[1] briefly described the action of a solution of potassium trinitride upon a neutral solution of the rare earths. It was found at that time that the flocculent precipitate which is produced was most probably thorium hydroxide, but our supply of potassium trinitride having been exhausted it was impossible to further investigate the reaction or ascertain the completeness of the separation. The immediate continuation of the work was prevented by unexpected difficulties which were encountered in the preparation of pure hydronitric acid on a large scale. These difficulties have since been removed, and it has been possible to prepare an amount of the reagent sufficient for the investigation described below.

[1] *Ztschr. anorg. Chem.*, 6, 35; *Am. Chem. J.*, 16, 79.

The solution of potassium trinitride which was used was prepared by carefully neutralizing a dilute solution of hydronitric acid with a dilute solution of pure caustic potash and then adding hydronitric acid sufficient to give to the solution a distinctly acid reaction. The solution first employed contained about three and two-tenths grams of potassium trinitride to the liter.

Before studying the separation of thorium from the other rare earths, the reaction between potassium trinitride and pure thorium chloride was first investigated. The thorium employed was from a sample of thorium oxalate, which had been very kindly presented to me by Dr. Theodor Schuchardt, of Goerlitz. It was found to be of a very high grade of purity, but to guard against the possible presence of other rare earths, the oxalate was converted to the oxide by ignition, treated with concentrated sulphuric acid, the anhydrous sulphate dissolved in distilled water at a temperature of 0°, and this solution was precipitated with pure oxalic acid. The precipitated thorium oxalate was thoroughly washed with hot water containing one per cent. hydrochloric acid, and was then dropped into a hot, concentrated solution of ammonium oxalate. It dissolved completely and no precipitate formed when the solution was diluted and cooled. From this solution the thorium was again precipitated as oxalate by means of strong hydrochloric acid and was then brought into solution as thorium sulphate in the manner described above. It was then precipitated by ammonium hydroxide and the precipitate thoroughly washed with water. The thorium hydroxide was then dissolved in hydrochloric acid, ammonium hydroxide was added until a faint but permanent precipitate remained, and this was then removed by filtration. There was thus obtained a neutral solution of thorium chloride containing a very small amount of ammonium chloride.

The strength of this solution of thorium chloride was ascertained by precipitating portions of ten cc. each with ammonium hydroxide, filtering, washing, igniting, and weighing as ThO_2. Two determinations gave, for thorium oxide in ten cc., 0.0591 gram and 0.0595 gram. The mean of these results is equivalent to 0.00521 gram thorium in one cc.

Upon adding to this thorium solution a few cc. of the solution of potassium trinitride, the precipitate which, in the previous work with Dr. Kortright, had formed at once, failed to appear; upon heating the solution to boiling, however, there was quickly formed a white, flocculent precipitate, closely resembling in appearance aluminum hydroxide, but settling rapidly when the flame was removed. In the first determinations the solution was boiled for five minutes, but it was later found that boiling for one minute is sufficient. During the boiling the odor of hydronitric acid was distinctly noticeable. The precipitate was washed by decantation with hot water, transferred to the filter, ignited, and weighed as ThO_2. Twenty cc. of thorium chloride, containing, according to the determination with ammonium hydroxide, 0.1186 gram thorium dioxide gave, by precipitation with potassium trinitride, 0.1183 gram thorium dioxide, equivalent to 0.00520 gram thorium in one cc. instead of 0.00521 as obtained with ammonia.

It is apparent, therefore, that thorium can be quantitatively precipitated by potassium trinitride.

The previous work of Dr. Kortright showed that the thorium is probably precipitated as the hydroxide, but the tendency of the precipitate to absorb carbon dioxide rendered the analyses unsatisfactory. If, however, the thorium is precipitated as the hydroxide, then all of the hydronitric acid of the potassium salt first added must reappear in the filtrate from the thorium hydroxide and in the gas evolved during the boiling. To ascertain whether this took place the precipitation was made in a round bottomed flask. In the neck of the flask there was inserted a two hole rubber stopper, through one opening of which a current of purified air was admitted, the other opening carrying an upright condenser. The condenser was connected at the upper end with two absorption vessels containing neutral silver nitrate solution. As the hydronitric acid was to be determined by precipitation with silver nitrate, a neutral thorium nitrate solution, containing 0.0075 gram thorium in one cc., was substituted for the thorium chloride. The thorium nitrate solution was placed in the flask, potassium trinitride was added, and after starting a current of air through the apparatus, the contents of the flask was heated to boiling and kept boiling for two minutes. Soon after the heating began a white precipitate of silver hydronitride formed in the first absorption flask containing the silver nitrate; by the time the reaction was complete this precipitate had become quite voluminous. The absorption of the gas by silver nitrate seems to be both rapid and complete, for nothing more than a slight opalescence ever appeared in the second absorption flask. After the apparatus had become cool the thorium hydroxide was filtered off and the filtrate was precipitated by silver nitrate. The silver trinitride thus obtained, together with that in the absorption flasks, was washed by decantation with cold water, the washings being passed through a hardened filter. When the wash water gave no further reaction for silver the funnel with the filter was placed in the neck of the flask containing the main part of the precipitate, and quite dilute, hot nitric acid was poured upon the paper. The silver trinitride on the paper dissolves almost immediately. After washing the paper with water, the funnel was removed and the contents of the flask was boiled until all of the silver trinitride had dissolved. The silver was then precipitated by hydrochloric acid and weighed as silver chloride. Ten cc. of thorium nitrate and ten cc. of potassium trinitride were used. The silver chloride resulting weighed 0.1447 gram, equivalent to 0.0434 gram hydronitric acid. The strength of the potassium hydronitride, which was a different solution from the one first employed, was then determined in the same manner.

5 cc. gave 0.0744 $AgCl = 0.02232\ HN_3$,
5 cc. gave 0.0745 $AgCl = 0.02235\ HN_3$.

Using the mean of these results, it appears that 0.0446 gram of hydronitric acid was used in the precipitation of the thorium nitrate, of which 0.0434 gram was recovered from the filtrate and distillate. That this latter result is somewhat low is doubtless due to the loss of hydronitric acid by volatilization during the filtration of the liquid in the flask. These results, together with those given in the preceding article already referred to, enable us to represent the reaction by the equation

$$Th(NO_3)_4 + 4KN_3 + 4H_2O = Th(OH)_4 + 4KNO_3 + 4HN_3.$$

This reaction is interesting not only because of the quantitative precipitation of thorium by this means, but also because of the peculiar behavior of the potassium hydronitride. As Ostwald has stated, hydronitric acid is but slightly stronger than glacial acetic acid, and the above equation reminds one of the behavior of acetates towards ferric iron, the solution of ferric acetate being fairly stable in the cold, but breaking down upon heating, into acetic acid and ferric hydroxide.

The experiments detailed below were then made to ascertain whether thorium could be quantitatively separated from the other rare earths by means of the above reaction. A neutral solution of pure lanthanum chloride was first prepared and its strength determined by precipitating with ammonium hydroxide and weighing the lanthanum as La_2O_3. The solution contained 0.00431 gram lanthanum in one cc. This solution gave no precipitate when boiled for some minutes with potassium trinitride. Fifteen cc. of this solution and fifteen cc. of the thorium chloride solution were placed in an Erlenmeyer flask, twenty-five cc. of potassium trinitride (three and two-tenths grams to the liter) was added and the solution was boiled 'or one minute. The precipitate was filtered off and washed with hot water, ignited, and weighed. To the filtrate five cc. more of potassium trinitride was added and the solution boiled for two minutes. No further precipitation resulted. The solution was then precipitated with ammonia and the lanthanum weighed as the oxide. The results were:

	Taken.	Found.
Thorium	0.0781	0.0777
Lanthanum	0.0646	0.0642

A mixture of the rare earths in Brazilian monazite was then freed from thorium by repeatedly digesting the mixed oxalates with a hot, concentrated solution of ammonium oxalate. The residual oxalates were then transformed into chlorides and dissolved in water. The solution showed the pink color and absorption bands of didymium and gave a strong reaction for cerium when treated with hydrogen peroxide and ammonia. When boiled with potassium trinitride it gave a very faint precipitate which was filtered off. By precipitation with ammonia this solution of cerium, lanthanum, didymium, etc., free from thorium, was found to contain 0.0166 gram of the mixed oxides in one cc. The precipitation was made as in the separation from lanthanum and an excess of potassium trinitride was used in each case.

		Taken.	Found.
I.	Thorium	0.1300	0.1294
	Ce, La, Di oxides	0.0332	....
II.	Thorium	0.0785	0.0783
	Ce, La, Di oxides	0.0830	....
III.	Thorium	0.0535	0.0526
	Ce, La, Di oxides	0.2490	....
IV.	Thorium	0.0535	0.0531
	Ce, La, Di oxides	0.2490	....
V.	Thorium	0.0550	0.0541
	Ce, La, Di oxides	0.4980	....
VI.	Thorium	0.0555	0.0550
	Ce, La, Di oxides	0.5810	....
VII.	Thorium	0.0570	0.0558
	Ce, La, Di oxides	0.8300	....

The recovery of the thorium is in all cases fairly exact and the variation in the relative amounts of thorium and the other earths does not influence the sharpness of the separation. That thorium alone is precipitated by potassium trinitride is to be explained by its weak basicity. It is the weakest base in the whole group of the rare earths with the possible exception of cerium in the ceric condition, and this higher form of cerium is probably incapable of existence in the presence of hydronitric acid.

We have, then, in potassium trinitride a reagent which can be used both for the qualitative detection of thorium and for its quantitative determination either alone or in the presence of other rare earths. So far as the author is aware, this is the only method as yet devised by which one of these earths can be quickly and accurately separated from the others, and that in a single simple operation.

CORNELL UNIVERSITY, August, 1896.

NOTES ON REINSCH'S TEST FOR ARSENIC AND ANTIMONY.

By Jas. Lewis Howe and Paul S. Mertins.

Received September 12, 1896.

THAT Reinsch's test for arsenic possesses, in point of convenience, marked advantages over that of Marsh, is generally acknowledged, but it has been questioned both as to delicacy and as to accuracy in distinguishing between arsenic and antimony. As to the former point, Reinsch, in his second article on the test,[1] states that arsenic may be detected in a solution of one part per million. In his original description[2] of the test he placed the accuracy about one-third of this. Our own experiments show that this accuracy is not overstated. The fact that arsenious oxide and antimonous oxide (Sb_2O_3) are isomorphous in their crystallization has led to the conjecture that antimonous oxide subliming from the copper in the closed tube might appear in the brilliant octahedra, characteristic of arsenic in the test.

Experiments bearing on this point were made as follows:

Reinsch's test was applied to the different compounds of arsenic in this laboratory and in each case several sublimation tubes were used. The test was carried out by boiling the substance with sixteen per cent. hydrochloric acid, in which several strips (2.5 × 0.5 cm.) of thin, pure copper were placed. After fifteen minutes (except in cases to be mentioned later) the strips of copper were removed, washed and dried, and after rolling or folding to small compass, placed in open tubes five cm. long and not over five-tenths cm. diameter. These tubes were held in an inclined position in the lowest possible flame of a Bunsen burner until the arsenic sublimed; a second or two usually suffices.

The test was similarly carried out with compounds of antimony and also with various organs of two cats, one killed by six grains of tartar emetic, dying six hours after administration, and the other dying in three days after the administration of the first of six small doses given every twelve hours. Each dose was two grains, but much of this was probably not taken into the system. A perceptibly higher degree of heat was necessary to

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[1] H. Reinsch: De l' Essai de l' Arsenic par le Cuivre: *J. pharm. Chim.*, 2, 361, (*1842*).

[2] H. Reinsch: Ueber das Verhalten des metallischen Kupfers zu einigen Metalllösungen: *J. prakt. Chem.*, 24, 244, (*1842*).

sublime the antimony than was the case with arsenic; altogether 185 tests were made, most of them furnishing good sublimation tubes. Each tube was numbered as made, and later the whole number were mixed and sorted for arsenic and antimony by examination with a microscope of low power. Reference to the note book showed that in no case had a mistake been made, in fact in every case the arsenic sublimation could easily be distinguished from that of antimony by the naked eye. In no case did the sublimate of antimonous oxide show a trace of crystallization under the microscope used, nor did the arsenious oxide fail in any case to show the characteristic brilliant octahedral crystals.

The evidence that the antimonous oxide cannot appear in crystals which might be mistaken for arsenic is of course negative, but owing to the variety of forms used it must be considered to have the weight of positive evidence.

As regards the substances tested, the following may be recorded:

All arsenious compounds soluble in hydrochloric acid gave the deposit on copper immediately on heating.

Commercial "metallic" arsenic gave the deposit readily.

Freshly sublimed "metallic" arsenic (bright crystals) gave no deposit.

Arsenates gave a deposit only after several minutes boiling.

In the presence of nitric acid or chlorates no test is obtained owing to the solution of the copper.

Whenever aqua regia or potassium chlorate is necessary for solution of an arsenic compound, the solution should be evaporated to dryness with hydrochloric acid. The test can then be carried out as with arsenates.

The presence of organic matter in the arsenic solution does not affect the test, hence it can be applied directly to any organs without any previous destruction of tissue. If much arsenic is present it is best to use but a small portion of the substance, since if much arsenic is deposited on the copper, it will not adhere with firmness.

Antimony is not precipitated on the copper as rapidly as arsenic, and the deposit has a decidedly violet tint, very distinct from the iron gray deposit of arsenic.

The following distribution of antimony in the two cats may be added:

Acute poisoning (6 hours).	Slow poisoning (72 hours).
Stomach.—Heavy deposit and sublimate. Good test with $\frac{1}{100}$ of stomach.	Good tests.
Liver.—Not so heavy deposit as stomach. Good sublimate.	Heavy deposit and good sublimate.
Heart.—Good deposit after several hours boiling. Good sublimate.	Good deposit on ninety minutes boiling. Good sublimate.
Pancreas.—Faint deposit. No distinct sublimate.	Good deposit and sublimate.
Spleen.—Faint deposit. No distinct sublimate.	
Kidney.—Faint deposit. No distinct sublimate.	Good deposit and sublimate.
Intestine.—Good deposit and sublimate.	Good deposit and sublimate.
Muscle.—Faint deposit on two days boiling. No sublimate.	Slight violet tinge to copper. No sublimate.
Brain.—No deposit.	Marked violet tint to copper. No sublimate.
Spinal Chord.—No deposit.	

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NOTES ON THE DETERMINATION OF PHOSPHORUS IN STEEL AND CAST IRON.

BY GEORGE AUCHY.

Received August 27, 1896.

OF the many improvements made in recent years in the method of determining phosphorus in steel, that of Jones—the use of the "reductor"—is not the least. There has been, however, some difference of opinion as to the completeness of the reduction accomplished by its use. Quoting from three most recent publications on the subject: Doolittle and Eavenson consider the reduction of the molybdic acid to be to a point corresponding to the ratio of 89.16 iron to molybdic acid ; Noyes and Royse, by special precautions, obtain a reduction completely to Mo_2O_3 (factor 85.71); and Blair and Whitfield find the ratio 88.16, a reduction to $Mo_{24}O_{37}$ only, even with the precautions of Noyes and Royse observed. Doolittle and Eavenson heat the solution before passing it through the reductor. Noyes and Royse do not. The first named chemists do not use the precautions of Noyes and Royse. It appears from a result by Prof. Noyes given in this Journal, 10, 759, that he does not invariably get a reduction to Mo_2O_3 by his method, his result there given corroborating Blair and Whitfield's hypothesis of a reduction to $Mo_{24}O_{37}$ only.

It was thought by the writer that perhaps the reduction to Mo_2O_3 could invariably be accomplished by combining the precautions of Noyes and Royse with the practice of Doolittle and Eavenson of passing the solution through the reductor hot. The following results were obtained, using yellow phosphomolybdate precipitate dried six hours at 150° C.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0100	1.63	1.63	1.68
0.0100	1.63	1.63	1.68
0.0200	1.63	1.59	1.63
0.0300	1.63	1.63	1.68
0.0300	1.63	1.61	1.65
0.0200	1.63	1.55	1.59
0.0400	1.63	1.59	1.63
0.0500	1.63	1.62	1.67
0.0500	1.63	1.63	1.68
0.0600	1.63	1.63	1.68
0.0700	1.63	1.61	1.65
0.0700	1.63	1.60	1.64
0.1000	1.63	1.63	1.68
0.0400	1.63	1.59	1.63
0.0400	1.63	1.59	1.63
0.0200	1.63	1.58	1.62
0.0400	1.63	1.56	1.60
0.0300	1.63	1.59	1.63
0.0900	1.63	1.57	1.61
0.0400	1.63	1.60	1.64
0.0500	1.63	1.61	1.65

Passing the solution through the reductor hot does not seem to insure an invariable reduction to Mo_2O_3, and perhaps adds nothing to the effectiveness of the process. The following tests were made in the cold :

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0500	1.63	1.58	1.62
0.0400	1.63	1.59	1.63
0.0300	1.63	1.59	1.63
0.0400	1.63	1.57	1.61
0.0500	1.63	1.63	1.68

But in these last tests, and also in the first series of tests in nearly all cases where the result calculated by Noyes' factor came low, the point of the reductor had been washed off, and the sides of the flask washed down by the jet. Noyes warns against any dilution of the reduced solution before titration, but it was thought that such a slight dilution would do no harm. For a test of this the following determinations were made (cold) and without washing down :

Phosphomolybdate taken. Gram.	Phosphomolybdate present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0500	1.63	1.61	1.65
0.0900	1.63	1.60	1.64
0.0300	1.63	1.61	1.65
0.0300	1.63	1.63	1.68
0.0400	1.63	1.60	1.64
0.0400	1.63	1.63	1.68
0.0300	1.63	1.63	1.68
0.0400	1.63	1.60	1.64
0.0400	1.63	1.63	1.68
0.0500	1.63	1.62	1.67

Comparing these results with those of the preceding series it is seen that a complete avoidance of any dilution, however slight, after reduction, will bring higher results than if this precaution be neglected. But it is further seen that the observance of this precaution does not invariably assure a result agreeing with a reduction to Mo_2O_3, although it generally does so. Of the eleven results in the first series of experiments (solution passed through the reductor hot), obtained by an observance of this precaution, seven, calculated by Noyes' factor, are over 1.61 ;

and of the ten results of the last series (reduced cold), seven are 1.61 per cent. or over. On the other hand, of the thirteen results obtained by washing down the sides of the flask after reduction, ten fall short of the theoretical 1.63 per cent. by more than 0.02 per cent., calculated by Noyes' formula, and do bring 1.63 per cent. calculated by Blair's factor. The inability of Messrs. Blair and Whitfield to accomplish a reduction to Mo_2O_3 by an observance of the precautions given by Messrs. Noyes and Frohman, and also the still higher factor found by Messrs. Doolittle and Eavenson, may perhaps be due to the fact that the zinc in each case used differed in reductive power from that of the others. The writer had on one occasion zinc which when used in the reductor with all care and precautions, never gave a reduction of more than one-half; and in his opinion it is safer and more accurate to use the old Emmerton method of reduction and filtration, but with the modifications and precautions described later in this article.

The phosphomolybdate employed in the above tests, was, for part of them, made by precipitating from sodium phosphate solution; for another part of the tests, made by precipitation from pig iron solution, exactly as is done in the determination of phosphorus in pig iron. Messrs. Blair and Whitfield have shown the constancy of the composition of phosphomolybdate made under varying circumstances.

The volume of the solution passed through the reductor in each of the above experiments was 100 cc., as recommended by Blair and Whitfield. Noyes and Frohman use 200 cc., but this seems an unnecessary bulk. Fifteen cc. of sulphuric acid (2:1) was used for acidifying.

For washing 100 cc. of hot water was used containing ten cc. of sulphuric acid, (2 : 1), followed by 100 cc. cold water, and again by fifty to seventy-five cc. of cold water.

The reductor was of the form described by Blair and Whitfield,[1] except that it was considerably wider at the top than the bottom—in shape like a common tin horn. This shape holds more zinc for the given height (ten inches) of the column, and so makes the necessity of filling less frequent.

[1] This Journal, 17, 74.

The reductor may be used without refilling till the column of zinc falls to five or six inches without any diminution of effectiveness. All of the results of the two preceding series, and some of the last results in the first series were obtained by the use of five to seven inches of zinc in the reductor.

It adds somewhat to the facility of the working of the apparatus to have the beaker containing the phosphorus solution above the level of the zinc in the reductor so that the connecting tube may work as a siphon. And the last washing may then conveniently be made by diminishing the force of the suction of the pump, loosening the stopper of the reductor, and allowing the water to be siphoned over and fill up the vacant space in the reductor above the zinc column.

The passage of the solution through the reductor was not preceded by the passage of dilute sulphuric acid, and in many of the tests some little air was accidentally drawn over into the reductor at the time of washing, although care was uniformly taken to allow no air to enter at the first washing.

Messrs. Noyes and Royse direct that the reductor should be rinsed with dilute sulphuric acid before using, even if it has stood but a few minutes. This is some little trouble, and to test the necessity of it, the following tests were made :

Phosphomolybdate taken. Gram.	Phosphorus taken. Per cent.	Phosphorus found. Per cent.	Reductor stood.
0.0300	1.63	1.61	one hour
0.0700	1.63	1.60	all night
0.1000	1.63	1.63	six hours
0.0300	1.63	1.63	all night
0.0300	1.63	1.63	three hours
0.0300	1.63	1.63	two days
0.0300	1.63	1.63	two days
0.0500	1.63	1.63	two days
0.0500	1.63	1.62	two days

These results seem an indication that this precaution is not absolutely necessary. But if the reductor stand nearly a week or more, the sulphuric acid will take up considerably more of the impurity of the zinc than ordinarily. Zinc, for instance, which ordinarily will require a deduction of two-tenths cc. from the amount of permanganate used in the titration, will require a deduction of four-tenths if the reductor has stood that length of time unused.

It is necessary to remove the zinc from the reductor at intervals for cleaning, best done by stirring up in a capacious dish with hot water, adding a little sulphuric acid to clear the liquid, pouring off, washing by decantation and drying in the dish on the hot plate. But after such a treatment the zinc, after being replaced in the reductor, should be rinsed with dilute sulphuric acid before being used in analysis, as much more than the ordinary impurity of the zinc will be taken up by the sulphuric acid the first time it is used.

Perhaps a more convenient way of cleaning the zinc is to soak it (in the reductor) in water for a day (conveniently over Sunday), plugging up the ends of the reductor to retain the water. After such a treatment the reductor will go a long time without becoming clogged up with zinc oxide.

Instead of using the reductor, it is a trifle quicker and more convenient,, especially when the phosphorus present is considerable as in pig iron, to use the following slight modification of the old Emmerton method of reduction and filtration.

The yellow precipitate in a seven cm. filter paper is dissolved in as little ammonia as possible, allowing to run into the eight-ounce Erlenmeyer flask in which the precipitation occurred; washed five minutes with hot water; the solution acidified with twenty-five cc. of sulphuric acid (two parts water to one part acid); a mustard spoonful of granulated zinc added (five grams), and the flask heated *gently* on the hot plate for five minutes, or until the zinc is nearly dissolved (ten minutes is required for some zinc). The flask is removed from the plate, a little dry sodium carbonate added, and when effervescence has nearly ceased the flask is corked tightly and cooled in cold water without agitating the contents any more than can be helped. The solution is then filtered from the undissolved zinc through a little cotton wool in a Hirsch funnel, smallest size, using the pump, and the flask rinsed out with cold water three times and the rinsings drawn through the cotton wool. The sides of the sixteen-ounce gas flask which receives the liquid are washed down with the jet, and the solution titrated in the flask without further dilution.

If the zinc is of the sort not dissolving very readily, thirty-five cc. of sulphuric acid should be used for acidifying the phosphorus solution instead of twenty-five cc.

The reduction is to $Mo_{12}O_{19}$. Factor of iron to molybdic acid 90.76. More correctly speaking, the reduction is to Mo_2O_3, which filtering and dilution oxidizes to $Mo_{12}O_{19}$.

It will be found upon trial that this way of reduction and filtration is somewhat easier and more rapid than the usual reductor method, as the filtration through cotton wool in a Hirsch funnel and with aid of the pump is performed as easily and quickly as merely pouring and rinsing from one vessel into another. While the zinc is dissolving in one determination, the yellow precipitate of the next determination may be filtered off.

The following results show that the reduction and filtration through cotton wool, as described, brings the molybdenum oxide to the form $Mo_{12}O_{19}$.

Considerable phosphomolybdate (four-tenths to eight-tenths gram) taken for each test.

Phosphorus present. Per cent.	Phosphorus found. Factor 90.76. Per cent.	Phosphorus present. Per cent.	Phosphorus found. Factor 90.76. Per cent.
1.63	1.63	1.63	1.63
1.63	1.63	1.63	1.62
1.63	1.62	1.63	1.63
1.63	1.63	1.63	1.63
1.63	1.63	1.63	1.62

Small amounts of phosphomolybdate taken.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Factor 90.76. Per cent.	Phosphorus present, reckoned as if from 1.8233 grams steel. Per cent. in the steel.	Phosphorus found if from 1.8233 grams steel. Per cent. in the steel.
0.2000	1.63	1.63	0.179	0.179
0.2000	1.63	1.63	0.179	0.179
0.2000	1.63	1.65	0.179	0.181
0.2000	1.63	1.63	0.179	0.179
0.1500	1.63	1.64	0.134	0.135
0.0890	1.63	1.62	0.071	0.071
0.0700	1.63	1.64	0.062	0.063
0.0700	1.62	1.63	0.062	0.062

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Factor 90.77. Per cent.	Phosphorus present, reckoned as if from 1.8233 grams steel. Per cent. in the steel.	Phosphorus found if from 1.8233 grams steel. Per cent. in the steel.
0.0600	1.63	1.64	0.054	0.054
0.0600	1.63	1.63	0.054	0.054
0.0500	1.63	1.61	0.045	0.044
0.0400	1.63	1.64	0.036	0.036
0.0300	1.63	1.64	0.027	0.027
0.0300	1.63	1.64	0.027	0.027
0.0300	1.63	1.61	0.027	0.027
0.0300	1.63	1.60	0.027	0.026
0.0400	1.63	1.62	0.036	0.036
0.0400	1.63	1.63	0.036	0.036
0.0400	1.63	1.63	0.036	0.036
0.0350	1.63	1.62	0.031	0.031
0.0380	1.63	1.63	0.034	0.034
0.0250	1.63	1.61	0.022	0.022
0.0230	1.63	1.61	0.020	0.020
0.0200	1.63	1.55	0.018	0.017
0.0200	1.63	1.51	0.018	0.017
0.0200	1.63	1.64	0.018	0.018
0.0200	1.63	1.50	0.018	0.017
0.0200	1.63	1.60	0.018	0.018
0.0200	1.62	1.55	0.018	0.017
0.0200	1.63	1.57	0.018	0.017
0.0180	1.63	1.55	0.016	0.015
0.0150	1.63	1.55	0.013	0.013
0.0150	1.63	1.55	0.013	0.013
0.0130	1.63	1.51	0.012	0.011
0.0120	1.63	1.63	0.010	0.010
0.0100	1.63	1.51	0.0089	0.008
0.0100	1.63	1.55	0.0089	0.0085
0.0100	1.63	1.46	0.0089	0.008
0.0100	1.63	1.64	0.0089	0.0089
0.0100	1.63	1.64	0.0089	0.0089

The figures in the last two columns were obtained by reckoning as though 1.8233 grams of steel had in each case been taken for analyses. In other words, these percentages in the last two columns are what they would have been had the phosphomolybdate taken been, in each case, obtained from 1.8233 grams of steel, in the regular course of analysis, for phosphorus.

It will be noticed that when the amount of phosphomolybdate taken is very small (equivalent to 0.008 to 0.017 per cent. in steel) there is frequently some oxidation, the percentage of phosphorus in the yellow precipitate thus falling short of 1.63 by as much as 0.17 per cent. in one case. But, as will be seen by reference to the last two columns of results, this affects the result in steel but slightly.

This proneness to oxidation when very little phosphorus is present in the solution indicates that the stability of the $Mo_{12}O_{19}$ solution is greater when concentrated than when dilute. And the solution should therefore be in as small bulk as possible. Other necessary precautions are: to have a large excess of sulphuric acid present, to avoid a boiling temperature when dissolving the zinc, to cool the liquid before filtering from the undissolved zinc, to exclude air while cooling, and to filter rapidly through cotton wool in a Hirsch funnel, with aid of the pump. But where considerable phosphorus is present, as in pig irons, these precautions may be neglected, except the cooling before filtering. That is, the liquid may be cooled, after the reduction with zinc, without the addition of sodium carbonate, and with free access of air, and the filtration may be made through a seven cm. coarse paper (instead of cotton wool) by aid of the pump. The results given under the head "considerable phosphomolybdate taken for each test" were obtained in this way, air not excluded, and filtered through paper instead of cotton wool.

The advantage of making the reduction and filtration in this way in the case of pig iron is very marked when, as frequently happens, the yellow precipitate separates out when its solution in ammonia is acidified with sulphuric acid. For if the reduction be made as described, this separation may be ignored as in contact with the zinc and sulphuric acid the yellow precipitate becomes reduced and goes into solution. This is shown by the following tests, in which no ammonia was used at all. That is, the yellow phosphomolybdate precipitate was weighed directly into the reducing flasks, and thirty-five cc. of sulphuric acid (2:1) poured over, a mustard spoonful of zinc added, heated gently, etc.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Per cent.
About 0.4000	1.63	1.63
" 0.4000	1.63	1.62
" 0.4000	1.63	1.63
" 0.4000	1.63	1.62
" 0.4000	1.63	1.63

In experimenting with this process some interesting results were had. The port wine $Mo_{12}O_{19}$ solution is apparently not so stable, especially in dilute solution or with small amounts of phosphorus present, as Emmerton supposed, and certain precautions are necessary.

In the first place considerable amounts of phosphomolybdate were taken, dissolved and reduced as described, and filtered through seven cm. filter papers by aid of the pump. The results showed 1.63 per cent. phosphorus, the theoretical amount.

Several tests were then made in the same way and with the same weights of yellow precipitates, but not waiting for the solutions to cool before filtering from the undissolved zinc. Instead of the theoretical 1.63 per cent., 1.57 per cent., and 1.58 per cent. were obtained, showing the necessity of filtering cold.

Next the stability of the reduced solution was tested.

Before filtering from the undissolved zinc.	Phosphorus present. Per cent.	Phosphorus found. Per cent.
Stood two hours	1.63	1.59
" " " and poured back and forth four times	1.63	1.55
Stood one hour	1.63	1.59
" one-half hour	1.63	1.61

The flasks were not corked while standing.

Smaller weights of phosphomolybdate precipitate were then taken. The results obtained fell very much short of the theoretical, 1.63 per cent., and varied considerably. It was at first thought that the filtration by aid of the pump oxidized the solutions more than by the original Emmerton way of filtering through a large ribbed filter. But, upon making four tests and filtering in that way (Emmerton's) the results gave 1.51 per cent., 1.52 per cent., 1.46 per cent., and 1.48 per cent., respectively, instead of the theoretical, 1.63 per cent., although about four-tenths gram yellow precipitate, was in each case taken; an amount of yellow precipitate which, when taken for the foregoing tests made by filtering through a seven cm. filter paper by aid of the pump, never failed of bringing a result equal to the theoretical. In filtering through a seven cm. filter by the pump the oxidation of the solution is therefore considerably less than the oxidation by filtering through a large ribbed filter.

An article by Blair and Whitfield[1] contains a description of an experiment made by reducing the phosphorus solution by boiling with zinc, keeping an atmosphere of hydrogen continually in the flask, and boiling till the zinc was completely dissolved; then cooling (maintaining the atmosphere of hydrogen in the flask) and titrating, the result falling considerably below the theoretical. In the case of the writer's low results just spoken of, obtained by filtering through a seven cm. filter paper by suction, the reduction had also been effected by boiling with the zinc, though not in an atmosphere of hydrogen, and not to complete solution of the zinc. Remembering the experiment of Blair and Whitfield, above quoted, it was thought that the reason for the low results in both cases lay, perhaps, in the boiling of the phosphorus solutions while being reduced, the sulphuric acid having an oxidizing effect perhaps in that case. No other reason could be offered at least for the low result in Blair and Whitfield's experiment, since, in that experiment, air had been so carefully excluded from the flask during the solution of the zinc and the cooling of the liquid. To test the matter, other determinations were made exactly as before, except that the zinc was dissolved at a gentle heat instead of by boiling. Results were much better, as will be seen in the following table. Hence the necessity for the precaution of avoiding a boiling temperature while dissolving the zinc.

Phosphorus present—1.63 per cent.

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[1] This Journal, 17, 757.

Phosphomolybdate taken. Gram.	Zinc dissolved by boiling. Phosphorus found.	Zinc dissolved at a gentle heat. Phosphorus found.
0.0100	1.37	1.55
0.0200	1.37	1.50
0.0200	1.37	1.41
0.0300	1.31	1.46
0.0300	1.37	....
0.0400	1.46	1.55
0.0500	1.39	1.57
0.0600	1.28	1.60
0.0700	1.52	1.57
0.0700	1.53	....
0.0800	1.16	1.57
0.2000	1.58	1.63
0.1000	1.59	1.64

In the second column of results, the third and fourth results are considerably lower than the rest of them. But it had been noticed that in these two determinations the green color of the reduced phosphorus solution had faded to the port wine shade during the cooling of the liquid and before the filtration from the undissolved zinc, while in all the other determinations the green color had persisted till the moment of filtration. This pointed to the necessity of excluding air during the cooling of the liquid, preparatory to filtration, from the undissolved zinc, and the precaution was accordingly adopted of corking the flask while cooling, first adding a little sodium carbonate to fill the flask with carbon dioxide. Results by this procedure follow.

As the flask is already filled with hydrogen gas from the solution of the zinc, and vapor from the heating of the liquid, it is perhaps unnecessary to add the sodium carbonate at the end of the reduction. In that case the flask should be corked with a one-hole cork with drawn-out glass jet, during the solution of the zinc; and the jet closed when the reduction is completed.

It was thought that results agreeing more closely and uniformly with the theoretical might be obtained by filtering through cotton wool instead of paper, as the filtration can be considerably more quickly accomplished in that way, even when much suction is used in the latter way. Results showed this to be the case, and are also given below in comparison with results by filtering through paper.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Filtration through paper. Phosphorus found. Per cent.	Through cotton wool. Phosphorus found. Per cent.
0.0100	1.63	1.41	1.55
0.0100	1.63	....	1.64
0.0100	1.63	....	1.46
0.0100	1.63	....	1.64
0.0100	1.63	....	1.46
0.0200	1.63	1.46	1.50
0.0200	1.63	1.48	1.60
0.0200	1.63	1.48	1.64
0.0200	1.63	....	1.63
0.0200	1.63	....	1.55
0.0200	1.63	....	1.57
0.0300	1.63	1.58	1.64
0.0300	1.63	1.57	1.63
0.0300	1.63	....	1.64
0.0300	1.63	....	1.61
0.0400	1.63	1.55	1.64
0.0400	1.63	....	1.62
0.0500	1.63	1.57	1.61
0.0600	1.63	1.57	1.64
0.0600	1.63	1.60	1.63
0.0700	1.63	1.60	1.63
0.0800	1.63	1.62	....

From these results it is seen that cotton wool is much better for use in filtering from the undissolved zinc than paper. Very little pressure is required with the former and very little cotton wool is required. A small Hirsch funnel is necessary. But the cotton wool should not be pressed down with the finger after it is wet, but sucked down by the pump. In the above experiments the filtrations through paper were also accomplished by a Hirsch funnel, smallest size. (Paper size, seven cm.)

Using cotton wool, no oxidation of the port wine, $Mo_{12}O_{19}$, solution need be feared where the amount of phosphorus present is that which in a sample of steel (one and eight-tenths grams) would be equivalent to 0.020 per cent. or over; while with percentages under 0.020 the oxidation is never greater than will make a difference of 0.001 per cent. in the result.

All the foregoing experiments were made with the use of zinc, requiring about ten minutes for solution. This supply becoming exhausted, new zinc was procured which happened to dissolve much more freely in acid, and experiments were therefore made as before but using only fifteen cc. of sulphuric acid for solution of the zinc instead of thirty-five cc. as before with the first lot of zinc. Results were noticeably lower, pointing to the inference that a large excess of sulphuric acid present is necessary as favoring the stability of the $Mo_{12}O_{19}$ port wine solution. Other determinations were then made, using twenty-five cc. of acid.

Phosphorus present, 1.63 per cent.

Phosphomolybdate taken. Gram.	Fifteen cc. sulphuric acid. Phosphorus found. Per cent.	Twenty-five cc. sulphuric acid. Phosphorus found. Per cent.
0.0400	1.63	....
0.0380	1.63	....
0.0350	1.62	....
0.0320	1.51	....
0.0300	1.55	1.60
0.0280	1.53	....
0.0250	1.50	1.61
0.0230	1.50	....
0.0230	1.55	1.61
0.0200	1.48	1.51
0.0200	1.55	1.55
0.0180	1.47	1.55
0.0180	1.48	....
0.0150	1.46	1.55
0.0150	....	1.55
0.0160	....	1.54
0.0140	....	1.56
0.0130	1.40	1.51
0.0100	1.40	1.51

This shows the necessity for the precaution of using plenty of sulphuric acid for solution of the zinc.

As before pointed out, results by the foregoing procedure, using all precautions, never fail of the theoretical, 1.63 per cent., or a reasonable approximation thereto, except when the amount of phosphomolybdate taken is only 0.0200 gram (equivalent to 0.018 per cent. in all steel determinations) or less, and the error in that case in a steel never amounts to more than 0.001 per cent. with about two grams of steel taken for analysis ; and the writer therefore, on the score of accuracy, prefers this method to the reductor method.

A convenience in phosphorus determinations is a Mohr burette for the sulphuric acid, attached to the sulphuric acid bottle by tubing reaching just to the zero mark of the burette according to the well known plan. The bottle should stand high, and the tubing be wide so that too much lung power will not be required to fill the burette. The delivery tube of the burette should also be of a good width, so that the acid may run quickly into the phosphorus solutions. The apparatus is also convenient for Elliott sulphur determinations, using sulphuric acid for acidifying the caustic soda sulphur solution instead of hydrochloric acid.

There is some difference of opinion among chemists as to the advisability of using sugar for reducing the manganese precipitate formed by the addition of permanganate to the boiling nitric acid solution of the steel. Sugar was originally recommended by Dr. Drown, but Mr. Clemens Jones, obtaining varying results which he attributed to its use, substituted ferrous sulphate with very satisfactory results. Dr. Dudley also states that in using sugar a different result is obtained than when ferrous sulphate is used. On the other hand, Handy and others have claimed that sugar has no harmful effect. The following tests were made by the writer:

No.	Using ferrous sulphate. Phosphorus. Per cent.	Using sugar. Phosphorus. Per cent.
Steel 618	0.017	0.018
" 620	0.018	0.018
Gray pig iron	0.719	0.720
Test bar	0.016	0.016
Steel 684	0.049	0.049
Phosphate solution	0.123	0.121

These results were considered sufficient evidence that sugar does not interfere with the precipitation of the phosphorus. Its use is more advantageous in several respects: it is cheaper than ferrous sulphate; less of it is required; it may be added to the boiling solution without fear of the solution boiling over; and it never contains phosphorus.

The merest pinch of sugar will suffice to reduce a very abundant precipitate of manganese peroxide if the boiling be continued for some time after its addition to the liquid.

For the filtration of the yellow phosphomolybdate precipitate with the aid of the pump, it is the writer's experience that nothing succeeds so well as two seven cm. Schleicher & Schüll No. 579 filter papers, folded and placed in the funnel together. The filtration may be made very rapidly, yet without any of the precipitate going through the paper.

After the solution of the yellow precipitate on the filter paper in ammonia and washing, the same filter may be used (without removal from the funnel) for another phosphomolybdate filtration, and so on for a number of consecutive determinations.

No. 579 is a very loose and porous paper. No. 589 *black ribbon* also serves.

SOME NEW COMPOUNDS OF THALLIUM.

BY L. M. DENNIS AND MARTHA DOAN, with Crystallographic Notes, by A. C. Gill.

Received September 4, 1896.

THALLOUS TRINITRIDE, TlN_3.

WHEN a concentrated solution of potassium trinitride containing a little free hydronitric acid is added to a solution of thallous sulphate, a white, finely crystalline precipitate is formed. This compound is soluble in hot water, and when recrystallized from a hot aqueous solution, it separates in orthorhombic needles of a light straw color.

The thallium in this salt was determined volumetrically by means of a standard solution of potassium permanganate, according to the method of Willm.[1]

In the case of the hydronitric acid, a volumetric method also was first attempted. A weighed portion of the salt was dissolved in water and placed in a Hempel distilling bulb, which was connected by fused joints to a condenser. A separatory funnel was inserted in the neck of the distilling bulb. The hydronitric acid was set free by the addition of an excess of dilute sulphuric acid and was distilled into an Erlenmeyer flask containing a known amount of ammonia, the excess of ammonia being then deter-

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[1] *Ann. chim. phys.*, (4), 5, 79.

mined by titration. It was at first difficult to drive over all of the hydronitric acid, the results being uniformly low with one exception, and in that case the distillate gave a reaction for sulphuric acid. The results continued poor in spite of various modifications which were tried, so that finally recourse was had to the gravimetric method, this not having been used before because of the explosive character of the silver trinitride. A weighed portion of the salt was dissolved in water and precipitated with a neutral silver nitrate solution. The silver trinitride was thoroughly washed by decantation with cold water, the washings being passed through a Schleicher and Schüll hardened filter No. 575. The precipitate was then transferred to the paper, the point of the filter carefully perforated and the precipitate washed through into a weighed porcelain crucible. Hydrochloric acid was then added to the contents of the crucible and the whole evaporated to dryness. By this treatment the silver trinitride is decomposed and the hydronitric acid expelled, together with the excess of hydrochloric acid. The silver chloride remaining in the crucible was then weighed, and from its weight the amount of nitrogen in the salt was computed. The results were:

		Calculated for TlN_3.	Found.
Thallium	204.18	82.9	82.87
Nitrogen	42.09	17.1	17.2
	246.27	100.0	100.07

The prism angle could be measured on the goniometer, but the end faces were too small to give good reflections. The trace of the macrodome on the prism face was measured repeatedly on the microscope stage, giving an angle of 51° 30′ with the vertical edge. The prism angle, $110 : \overline{110} = 79° 50'$. Hence the axial ratio:

$$\breve{a} : \bar{b} : \acute{c} = 0.8366 : 1 : 1.2407.$$

The crystals were composed of many fine needles, sometimes twinned on the prism face (110), but more frequently in parallel growth. The double refraction was strong, and the plane of the optical axes is at right angles to the long direction of the needles, *i. e.*,= 0.001.

Thallous trinitride is somewhat soluble in cold water and is easily soluble in hot water. It is not explosive, resembling in this particular the trinitrides of potassium and sodium. It melts without decomposition when heated in an atmosphere of carbon dioxide. Its melting point was determined by placing some of the crystals in a small glass tube in the top of which was inserted a cork with two holes. Carbon dioxide was passed into the tube through one of these openings, and a small exit tube was inserted in the other. The tube was heated by immersing it in a bath containing an easily fusible alloy, and the temperature was measured with a carbon dioxide filled thermometer corrected by the Physikalisch-Technische Reichsanstalt of Charlottenburg. The corrected temperature at which the crystals melted was 334°.

When exposed to the sunlight, the crystals of thallous trinitride assume a dark brown appearance, which is probably due to the formation of thallous oxide. This change must be very superficial, however, as no change in weight could be detected in a sample which had been in a southern exposure for two months.

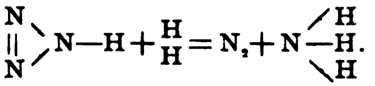
When heated in a current of dry nitrogen, thallous trinitride was easily reduced. The hydrogen on leaving the combustion tube, in which the boat containing the thallous trinitride was placed, was passed through two bulbs containing water. The aqueous solution thus obtained had a very distinct odor of ammonia, turned turmeric paper brown, and when neutralized with hydrochloric acid and allowed to spontaneously evaporate over sulphuric acid and caustic potash, it yielded crystals which under the microscope were identical with those of ammonium chloride. The ammonia found in two of the reductions in hydrogen was titrated with standard acetic acid, this acid being used in order that only the free ammonia might be neutralized and any ammonia which might be present combined with hydronitric acid would remain as such.[1]

In one case 29.83 per cent. of the nitrogen in the trinitride acid was converted into ammonia; in the other 27.37 per cent. of the nitrogen was thus changed.

[1] HN_3 is somewhat stronger than glacial acetic acid. *J. prakt. Chem.*, (2), 43, 207.

Hydronitric acid was tested for in the aqueous solution by addition of silver nitrate to the solution in which the ammonia had been neutralized, and in each case only a trace was found. It was thought that perhaps the formation of the acid might be due to the presence of a small amount of moisture in the hydrogen, so a reduction was made with hydrogen which had been passed through a piece of moist cotton. In this case 21.55 per cent. of the nitrogen was converted into ammonia, and as before only a small amount of hydronitric acid was formed.

The highest results for the nitrogen converted into ammonia approximate one-third of the total nitrogen present, and inasmuch as only a trace of the nitrogen is found to exist in the form of hydronitric acid, it is possible that the molecule of the acid breaks down thus :[1]



THALLOUS THALLIC TRINITRIDE, $TlN_3.TlN_3$.

It was thought that thallic trinitride might be obtained by the solution of freshly precipitated thallic hydroxide in hydronitric acid. The hydroxide when treated with hydronitric acid and warmed, dissolved to a clear straw-colored solution, but when the solution was allowed to stand at ordinary temperature, hydronitric acid escaped and thallic hydroxide was precipitated. Concentration of the solution was tried by placing it in a freezing mixture and removing the water as ice. From the liquid thus concentrated, bright yellow crystals separated, yet so much of the salt solution was occluded in the ice that this method proved wasteful. The best yield of crystals was obtained by dissolving the thallic hydroxide in a one and six-tenths per cent. solution of hydronitric acid and allowing the solution to stand at a temperature of about zero in a Hempel desiccator which was exhausted by means of a common suction pump. Glistening, yellow, needle-shaped crystals appeared. They were removed in five fractions, which under the microscope seemed to be alike and homogeneous.

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[1] The further investigation of this reaction is now being carried on in this laboratory. D.

These sharply outlined crystals verged toward a brown color in the larger specimens. On the stage of a microscope they showed either parallel extinction, or an extinction of 42°. That is, the long direction of the crystals varied in different individuals. The crystals were probably triclinic, though there is a possibility that they furnished a case of flattening, parallel to the face of the orthorhombic pyramid. An optical axis emerged obliquely from the tabular face, showing that it was not really, as would otherwise appear, the pinacoid of an orthorhombic crystal. The plain angles were 132°, 132° and 96°. The double refraction was not very strong.

The thallium was determined by dissolving some of the crystals in dilute hydrochloric acid, reducing the thallium to the thallous condition by sulphurous acid, driving off the excess of the latter acid by heating the solution and then titrating with potassium permanganate. The nitrogen could not be determined by the method used for thallous trinitride, because the salt could not be dissolved either in water or dilute acids without evolution of hydronitric acid. For this reason the absolute method was used. We had already found that the salt was highly explosive, but the behavior of the thallous trinitride, when heated in an atmosphere of carbon dioxide, led us to attempt the decomposition of a small portion of this substance in a similar manner. A few milligrams were, accordingly, spread over the bottom of a long porcelain boat, which was placed in a combustion tube containing granular copper oxide. The tube was connected at one end to a carbon dioxide generator, and at the other to a Schiff nitrometer. The exit end of the tube was heated to redness and the heat was then run back very carefully toward the boat. Gradual decomposition of the compound, however, was not attained, for when the temperature in the neighborhood of the boat had risen but slightly, the salt exploded violently, shattering the boat and tube. Another portion of the hydronitride was then mixed with granular copper oxide and heated as before. The decomposition in this case was quiet and gradual. The nitrogen in the nitrometer amounted to 27.32 per cent. of the salt taken. It seemed possible, however, that in mixing the hydronitride with the coarse copper oxide, some of the salt might have been decomposed by the friction, and that consequently the above per cent. of nitrogen might be too low. To ascertain if this were true, a fresh portion of copper oxide was ground very fine and was then carefully mixed with a small portion of the salt. In this way higher results were obtained.

The analysis gave:

		Calculated for TlN_6.	Found.
Thallium	204.18	70.81	70.70
Nitrogen	84.18	29.19	29.3
	288.36	100.00	100.00

If this were a simple compound, the thallium would seem to be in the bivalent condition, but as this is at variance with the usual behavior of the element, it seemed more probable that the compound is a double salt containing thallium in both the thallous and thallic condition. This supposition was confirmed by the behavior of the crystals when treated with hot water. Brown thallic hydroxide separated, and upon filtering this off and adding potassium iodide to the filtrate, a precipitate of thallous iodide resulted. Instead, however, of finding only fifty per cent. of thallium in the thallous condition, as would be required by the formula $TlN_3.TlN_9$, there was obtained 63.7 per cent. This excess of thallous thallium is doubtless due to the reduction of some of the thallic hydroxide by the hydronitric acid set free when the salt is treated with hot water.

Thallous-thallic trinitride is highly explosive, the decomposition being accomplished by a sharp report and a vivid flash of green light. The explosion can be brought about by heat, percussion or even gentle friction.

THALLOUS TELLURATE, Tl_2TeO_4.

In 1878 F. W. Clarke prepared what he supposed to be thallous tellurate by precipitating a thallous nitrate solution with ammonium tellurate.[1] The amount obtained was so small that no analysis was made.

To avoid the presence of other salts in the solution, we used a solution of thallous hydroxide and precipitated that by adding a

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[1] *Ber. d. chem. Ges.*, 11, 1507.

solution of pure telluric acid. The white, flocculent precipitate which formed was washed with cold water, transferred to a filter and dried over calcium chloride.

In the analysis of this substance, the thallium was determined by the method above described. Considerable difficulty was encountered in the determination of the tellurium, the presence of thallium making it impossible to use either the potassium permanganate titration or the method recently described by Gooch.[1] The thallous tellurate was soluble in water, but the amount of water required for its solution was so great that the telluric acid could be precipitated by neither lead nor barium solutions. For these reasons the method of Kastner[2] was used, the tellurium being precipitated in alkaline solution by means of grape sugar. As some thallium separated with the tellurium, the precipitate was treated with nitric acid and the acid then driven off by evaporation. The thallous nitrate was removed by washing the residue with water and the tellurous oxide was filtered in a Gooch crucible, dried and weighed. The results were :

		Calculated for Tl_2TeO_4.	Found.
Thallium	408.39	68.13	68.17
Tellurium	127.00	21.19	21.19
Oxygen	64.00	10.68 (diff.)	10.64
	599.36	100.00	100.00

Thallous tellurate is slightly soluble in water, and it was hoped that there might be obtained from the aqueous solution crystals sufficiently well defined to admit of a comparison of them with those of thallous sulphate and thallous selenate. Unfortunately, however, it was found impossible, in spite of many and varied attempts, to obtain anything but a white amorphous powder. Even when a solution saturated at 40° was allowed to slowly cool to 15° through a period of eight days, no crystals resulted.

THALLOUS CYANPLATINITE, $Tl_2Pt(CN)_4$.

Carstanjen prepared what he reported to be thallous cyanplat-

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[1] *Ztschr. anorg. Chem.*, 7, 132.

[2] *Ztschr. anal. Chem.*, 14, 142.

inite by neutralizing cyanplatinous acid with thallous carbonate.[1] The compound was given the formula TlCN.PtCN, although no analytical results were given.

The cyanplatinous acid used by us in the preparation of the thallium cyanplatinite was obtained according to the method of Schafarik.[2] It was neutralized by thallous hydroxide, which was prepared by precipitating a thallous sulphate solution with the calculated amount of baryta water. The crystals separated out in the form of thin plates.

A determination of the thallium and cyanogen gave the following results:

		Calculated for $Tl_2Pt(CN)_4$.	Observed.
Thallium	408.36	57.73	57.7
Platinum	195.00	27.56	...
Cyanogen	104.12	14.71	14.5
	707.48	100.00	

The crystals are nearly colorless plates, usually very thin and occurring irregularly grown together on the flat sides. The crystal system was not positively determinable from the material at hand, but is probably triclinic, possibly monoclinic with crossed dispersion. In converged polarized light, a bisectrix is seen nearly or quite normal to the large face of the plates, and the dispersion of the planes of the optic axes is remarkably strong, so that the crystals simply change color without becoming dark on rotation between crossed Nicols. The double refraction is high. The plates are bounded by crystal faces, giving them a six-sided outline, but on the material used no goniometric measurements could be made.

CORNELL UNIVERSITY,
AUGUST 1896.

[1] *J. prakt. Chem.*, 102, 144.

[2] *Ibid.*, 66, 401.

NOTES ON THE ESTIMATION OF CAFFEIN.

BY W. A. PUCKNER.

Received September 2, 1896.

SOME time ago Gomberg published a method for the estimation of caffein, by means of Wagner's reagent,[1] wherein appear certain statements from which is to be inferred the superiority of this method over such where the caffein is shaken out of an aqueous solution by means of chloroform, and which, if true, would show that most methods now in use, give low results since but an imperfect separation of caffein is attained. Thus Spencer[2] is said to have demonstrated the difficulty with which the alkaloid is abstracted from watery solutions, he directing that at *least* seven portions of chloroform be used for this purpose, but offering no proof of the necessity for this departure from the usual direction of shaking out the liquid with three or four portions of the solvent. Spencer is at variance with Allen,[3] who investigated this matter and found that from a solution, slightly acidulated with sulphuric acid, one treatment with chloroform removed seventy to eighty-five per cent. of the amount present, while four usually effected complete extraction, especially if toward the end the solution is rendered faintly alkaline.

This agrees well with the results of my own experiments, where anhydrous caffein, in quantities from one-tenth to four-tenths gram, dissolved in fifty cc. one per cent. sulphuric acid, was shaken successively with twenty-five, ten and ten cc. chloroform, the united chloroform solution evaporated at a gentle heat and the residue dried over sulphuric acid to constant weight. In each case the solution was shaken with a further quantity of ten cc. chloroform and the weight of the caffein so extracted ascertained as before.

Caffein taken. Gram.	Residue from first, second and third extraction. Gram.	Residue from fourth extraction. Gram.	Total per cent. recovered.
0.1285	0.1277	0.0004	99.69
0.1852	0.1820	0.0026	99.67
0.1988	0.1980	0.0002	99.69
0.2011	0.1977	0.0025	99.55
0.2559	0.2552	0.0005	99.92
0.4416	0.4355	0.0043	99.58

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[1] This Journal, **18**, 331.

[2] *J. Anal. Chem.*, **4**, 390.

[3] Com. Org. Anal., **3**, Part II, 485.

This shows that the extraction of caffein from an aqueous solution presents no difficulties since, even when the solution is quite acid, practically the entire amount is obtained when four portions of chloroform are used; while, even if the fourth be omitted the results will be sufficiently correct for most purposes.

In the article referred to we are also told, although it is usually stated caffein may be shaken out of an acid solution, since its salts are broken up by water, that this is but relatively true; as a proof thereof the following is offered:

" 1.0085 grams of caffein were dissolved in sixty cc. of sulphuric acid (1.10), and this solution was repeatedly shaken with chloroform, twenty-five cc. at a time:

Ten consecutive portions of chloroform gave a total of 0.3514 gram caffein.
Three additional " " " made " " 0.4859 " "
Three more " " " " " " " 0.5034 " " "

Since the degree of dissociation of caffein salts is inversely proportional to the acid strength of the solution, it is to be expected that it will be extremely difficult to shake out the alkaloid from a solution containing so great a quantity of free acid; but while at times it may be advantageous to extract caffein from a solution having an acid reaction, in no instance would there seem need of a sufficient amount to render the method inapplicable; further, according to Knox and Prescott[1] Gomberg's method becomes uncertain under similar conditions.

In the experiments just quoted ten extractions with chloroform yielded but 34.85 per cent. of the total caffein, or on an average each treatment removed only 3.485 per cent., while the three subsequent treatments removed an additional 13.33 per cent. of the whole, or 4.44 per cent. for each extraction, *i. e.*, although the total substance in solution had been decreased by more than one third the average amount given up to chloroform increased in the 11th, 12th and 13th treatment; while in the 14th, 15th and 16th but 1.735 per cent., or on an average of 0.578 per cent. for each shaking was obtained.

Although the writer had never attempted a caffein determination under the conditions mentioned, he was, from theoretical considerations, inclined to question the figures given, and accordingly made the following experiments.

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[1] Proceedings Am. Pharm. Ass., *1896*.

1.0137 gram caffein, rendered anhydrous by keeping in a desiccator over sulphuric acid until its weight remained constant, was dissolved in sixty cc. ten per cent. sulphuric acid and shaken successively with nine portions of chloroform, twenty-five cc. each ; the chloroform solutions evaporated at a gentle heat and the residue dried over sulphuric acid to constant weight.

1st portion of twenty-five cc. yielded a residue of	0.5525 gram.
2nd " " " " " " " "	0.2514 "
3rd " " " " " " " "	0.1155 "
4th " " " " " " " "	0.0535 "
5th " " " " " " " "	0.0237 "
6th " " " " " " " "	0.0114 "
7th " " " " " " " "	0.0058 "
8th " " " " " " " "	0.0029 "
9th " " " " " " " "	0.0015 "
	1.0182[1] "

In the second experiment 1.0001 gram anhydrous caffein in sixty cc. ten per cent. sulphuric acid, extracted as before, with chloroform in proportions of twenty-five cc. each :

1st, 2d and 3rd portions gave a total residue of	0.9086 gram.
4th, 5th and 6th " " " " " "	0.0854 "
7th, 8th and 9th " " " " " "	0.0134 "
	1.0074[1] "

The sulphuric acid used in Gomberg's experiments was designated as "(1:10)" by which it is presumed an acid containing ten per cent. by weight of sulphuric acid was meant; since, however, it was possible that sulphuric acid 1:10 *by volume* was the strength of the acid used, a determination was made with an acid with such concentration, *i. e.*, ten cc. concentrated sulphuric acid mixed with water enough to make when cold, 100 cc. In sixty cc. of this were dissolved 0.9790 gram caffein and extracted with chloroform in portions of twenty-five cc. each as before.

1st, 2nd and 3rd portion yielded a total residue of	0.6484 gram.
4th, 5th and 6th " " " " " "	0.2222 "
7th, 8th and 9th " " " " " "	0.0756 "
10th, 11th, 12th, 13th, 14th, 15th and 16th " "	0.0379 "
	0.9841[1] "

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[1] No explanation is offered to account for the plus error in the above. Contamination with sulphuric acid was suspected, but disproved.

As was to be expected, this confirms in a general way, the statement relative the difficulty with which caffein is shaken out of solutions containing a large proportion of sulphuric acid; in no way, however, does it agree with the data given by Gomberg, who by ten successive treatments with chloroform removed only 34.85 per cent., while my figures show that when a ten per cent. sulphuric acid was used, with but three extractions, fully ninety per cent. was recovered, and even with a still stronger acid (1 + 9 by volume), three portions of chloroform removed about sixty-five per cent.

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CONTRIBUTION TO THE KNOWLEDGE OF THE RUTHENOCYANIDES.

BY JAS. LEWIS HOWE.

Received August 27, 1896.

POTASSIUM ruthenocyanide was described by Claus, in 1854, in his "Beiträge zur Chemie der Platinmetalle." The salt was formed by fusing ammonium rutheninitrosochloride[1] (tetrachloride of Claus) with potassium cyanide. The attempt was also made to form it by fusing potassium ferrocyanide with ruthenium, but it was found impossible to separate the ferrocyanide and ruthenocyanide. It is probable that some of Claus' experiments were carried out with a ruthenocyanide contaminated with ferrocyanide, from the fact that he describes copper ruthenocyanide as brown, whereas, when free from the ferrocyanide, it is pale green. Potassium ruthenocyanide in reactions and crystallization resembles very closely the ferrocyanide, except that when pure it is white. Its crystallography as well as that of the isomorphous ferrocyanide and osmocyanide are described by A. Dufet.[2]

Preparation of potassium ruthenocyanide for the purpose of carrying out experiments upon it not yet completed, gave occasion to the work recorded in this paper.

In the Claus method of preparation, a large proportion of the ammonium rutheninitrosochloride is decomposed with separation of metallic ruthenium, and while a part of the ruthenocya-

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[1] Joly: *Compt. rend.*, 108, 854, *1889*; Howe: *J. Am. Chem. Soc.*, 16, 388, *1894*.

[2] *Compt. rend.*, (*1895*), 120, 377.

nide formed crystallizes out from a solution of the melt, in large square pseudorhombic plates, much is left in the solution and cannot be directly separated from the potassium cyanide and other salts present. Attempts were therefore made to use other methods of formation with the following results :

1. Potassium rutheninitrosochloride, K_2RuCl_5NO, fused with potassium cyanide, gave rather better results in ruthenocyanide, there being rather less decomposition than was the case with the ammonium salt.

2. Ruthenium trichloride, $RuCl_3$, fused with potassium cyanide gave a fair product of ruthenocyanide.

3. Metallic ruthenium, fused with potassium cyanide, was slightly acted upon, giving a trace of ruthenocyanide.

4. Metallic ruthenium, fused with potassium cyanide and a little potassium hydroxide, gave rather stronger reaction than case 3, but the amount of ruthenocyanide formed was very small.

5. The melt formed by fusion of ruthenium in potassium hydroxide and nitrate, containing potassium ruthenate, K_2RuO_4, was dissolved in water and boiled with potassium cyanide. The deep orange-red solution was quickly decolorized and the ruthenium was converted into ruthenocyanide with little loss. A considerable proportion could be obtained in the usual square crystals. This process could, by modification, probably be made the most satisfactory method of forming the ruthenocyanide, presenting one decided advantage that metallic ruthenium, or oxides, can be used, thus avoiding the necessity of preparing the nitrosochloride or chloride.

6. Ruthenium trichloride was boiled with a strong solution of potassium cyanide. The ruthenocyanide, crystallizing in the usual square form, was obtained, but very much contaminated with a greenish by-product not yet investigated, probably analogous to Prussian blue.

7. Potassium rutheninitrosochloride was boiled with a strong solution of potassium cyanide. The solution was slowly decolorized, considerable of the greenish by-product being formed. From this solution there crystallized thick straw-colored hexago-

nal plates, which will be considered further on. The quantity of the product is not satisfactory.

8. The Weselsky method[1] of forming double cyanides was tried. Hydrocyanic acid was led into a solution of the nitrosochloride, in which barium carbonate was suspended, until effervescence ceased. The solution gave no reaction for ruthenocyanide. Its color had changed to the brown-yellow of the trichloride, but gave no reaction for this with potassium thiocyanate, or with ammonia and sodium thiosulphate. On warming, the solution gelatinized to a firm hydrogel, insoluble in hot aqua regia, but soluble in boiling potassium hydroxide. This last solution was unchanged on acidification with hydrochloric acid, and gave the potassium ferrocyanide reaction for nitrosochloride, but no reaction for trichloride. The dried jelly was easily explosive on heating. It presents an interesting analogy to Jackson's[2] hydrogel of cobaltocyanide and is being further studied.

9. The Weselsky method was also applied to ruthenium trichloride. The merest trace of ruthenocyanide was formed, and the solution, little changed in color, no longer gave reactions for the trichloride.

10. The nitrosohydroxide of Joly, formed by the precipitation of the chloride by potassium carbonate, is easily soluble in potassium cyanide and converted into ruthenocyanide by prolonged boiling.

The following reactions of ruthenocyanide may be noted:

No precipitates are formed with the caustic alkaline earths, their ruthenocyanides being soluble in water.

Lead acetate gives a fine white precipitate, soluble in nitric acid.

Silver nitrate gives a white curdy precipitate, insoluble in both ammonia and in nitric acid.

Ferric chloride gives a rich purple precipitate, closely resembling Prussian blue in its chemical properties. In pure water it is soluble, but is precipitated from this solution by salts or alcohol. It forms a very beautiful and intense dye, adhering with

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[1] Weselsky, Sitzber. Akad. Wien., 60, ii. (*1870*), 261; *Ber. d. chem. Ges.*, 2, 588, *1869*.

[2] Jackson: *Ber. d. chem. Ges.*, 29, 1020, *1896*.

great persistence to cotton fiber, on which it has been precipitated. It is decomposed very readily by alkalies with precipitation of ferric hydroxide, re-forming, however, on the addition of acids, unaffected by dilute acids, but permanently decomposed by strong acids. It is a most delicate reaction for the detection of ruthenocyanide.

Ferrous sulphate gives a pale blue precipitate, which gradually changes to the purple above mentioned, and instantly if bromine water is added.

Copper sulphate gives a very pale green flocculent precipitate (not brown as given by Claus).

With salts of the following metals precipitates are formed insoluble in hydrochloric acid : Cadmium, white (soluble in hot acid) ; zinc, white ; tin (both stannous and stannic), white ; mercury, white ; bismuth, white (insoluble in nitric acid) ; nickel, dirty green (changing to blue with hydrochloric acid) ; cobalt, pale red ; platinum, yellow-green ; manganese gives a white precipitate soluble in hydrochloric acid. With gold there is no immediate precipitate, but a gradual darkening and separation of a dark precipitate, the solution becoming green.

Bromine water changes the solution to a dark red, which does not give the trivalent ruthenium reaction. Iodine also seems to alter the solution.

No reaction with hydrogen sulphide, ammonium sulphide, or thioacetic acid.

Nitric acid has no effect in the cold, but when heated slightly reddens the solutions. It then shows no signs of a reaction analogous to that of the nitroprussides.

It is acted on by potassium nitrite with sulphuric acid, and when neutralized gives a fugitive rose red with ammonium sulphide.

It gives no apparent reaction with ruthenium trichloride or nitrosochloride.

Two methods of purification, applicable to such portions of the ruthenocyanides as cannot be separated by crystallization, may be used. The most satisfactory is the precipitation in dilute solution by lead acetate and thorough washing with hot water to remove any lead chloride present. Suspension of the lead ruthenocyanide (carbonate, cyanide, etc.) in much water and decomposition with dilute sulphuric acid. Filtration and addition of baryta water till nearly neutral and then of barium carbonate in excess; warming, filtration, and evaporation to crystallization of the barium ruthenocyanide from which other ruthenocyanides may be formed by double decomposition.

The other method of purification which is applicable especially to all residues, is precipitation with ferric chloride in slightly acid solution, washing with acidified water, as far as possible (the purple begins to dissolve as the salts are washed out) and decomposing with baryta water. This method, while very useful for recovery of residue, does not give so pure a product as the first method.

The hexagonal crystals described above, in process 7, presented points of interest, in that it seemed not impossible that they contained the nitroso group of the nitrosochloride from which they were formed. When dissolved in water they showed every reaction of the ordinary square crystals of the ruthenocyanide, but they could not be converted into the square form by recrystallization nor could their yellowish tint be removed. The crystals are anhydrous while the white crystals contain three molecules of water of crystallization. On heating they explode with considerable violence while the square crystals decompose very gently. On recrystallization they show prismatic forms, with many twins resembling staurolite crosses, and others resembling aragonite twins. Though perfectly hexagonal in form, they do not seem to belong to the hexagonal system. After conversion into the lead, hydrogen, barium, and back into the potassium salt by the first method of purification described, and further precipitation of this potassium salt by alcohol and recrystallization from water, crystals were obtained which were square, white, and in every respect, crystallographically as well as chemically, resembled the ordinary potassium ruthenocyanide. This was verified by analysis of the barium salt and partial analysis of the potassium salt.

It is evident that the hexagonal crystals are not a nitrosocyanide, and it seems possible that the form may be conditioned by some trace of impurity. They are being further studied at present.

ANALYSIS OF POTASSIUM AND BARIUM RUTHENOCYANIDES.

Potassium ruthenocyanide, $K_4Ru(CN)_6,3H_2O$, formed by boiling a solution of potassium rutheninitrosochloride with potassium cyanide; purified by conversion through lead, hydrogen, and barium salts.

		Per cent.
I.	Loss of water in four days standing over sulphuric acid	10.84
II.	" " " at 120°	10.90
III.	" " " in 30 hours standing over sulphuric acid	11.25
	Theory for $K_4Ru(CN)_6,3H_2O$. $3H_2O$ =	11.53

The crystals, especially when small, are so efflorescent that it is difficult to obtain uneffloresced salt for analysis, and the following are calculated for the dehydrated salt.

	Theory for $K_4Ru(CN)_6$.	Found. I.	II.	III.
Potassium	37.76	37.22	38.32	37.28
Ruthenium	24.53	23.90	24.22	24.44

This corresponds to the potassium ruthenocyanide described by Claus.

Barium ruthenocyanide, $Ba_2Ru(CN)_6,6H_2O$, (new) formed from the ordinary form of the potassium salt.

Pale straw-colored, diamond-shaped (up to one-half cm. long) monoclinic crystals, or larger crystal rosettes, slightly soluble in cold, more easily in hot water, slowly lose water of crystallization over sulphuric acid, lose five and a half molecules of water at 100° but retain one-half molecule to nearly 200°, thus resembling barium ferrocyanide. The barium ruthenocyanide from the hexagonal form of the potassium salt was similar, but was not obtained in well enough defined crystals to identify positively with the preceding, but analysis shows the constitution to be the same.

The method of analysis was the following: The salt was heated in a platinum boat (in two cases porcelain was used and attacked, so that the ruthenium was contaminated by silica—Analyses I and V) in an oxygen current, and the carbon dioxide evolved collected in an absorption apparatus. The proportion given off was variable, but usually a little more than five atoms. The boat was then heated in a hydrogen current, to reduce the oxide of ruthenium formed. The boat was then placed in a carbon dioxide apparatus and treated with hydrochloric acid and the remainder of the carbon dioxide collected. The barium chloride was then filtered off from the ruthenium and determined as sulphate; the ruthenium, after burning the filter paper and heating in a hydrogen current in a porcelain boat, was estimated as the metal. It was not found possible to arrive at any agreement in different analyses as to the loss on heating the barium salt in air, or oxygen, or subsequently in hydrogen. While most of the carbon of the cyanogen is burned to carbon dioxide, a part remains as barium carbonate. The remainder of the barium seems to fluctuate between oxide and peroxide, while a variable portion of the ruthenium is oxidized. The analyses show conclusively that six atoms of carbon are present in the salt derived from the nitrosochloride, hence one cyanogen group cannot be replaced by the nitroso group.

The results of several analyses are as follows:

		Found.						
	Theory for $Ba_2Ru(CN)_6.6H_2O$.	From $RuCl_3$ and KCN sol.	From $RuCl_3NO$ by fusion.			From $RuCl_3NO$ by solution.		
		I.	II.	III.	IV.	V.	VI.	VII.
Barium	42.90	....	....	....	42.46	43.32	42.27	42.54
Ruthenium	15.86	16.41 (with SiO_2)	15.67	....	15.72	17.92 (with SiO_2)	15.80	15.60
$5\frac{1}{2}H_2O$ (100°)	15.67	15.67	15.63	....	15.68	....	....	15.53
$6H_2O$ (200°)	16.83	16.68	16.85	...	16.69	16.71	16.56	16.68
5 C	9.37	....	....	....	....	....	....	....
6 C	11.23	....	....	....	....	....	....	....
C from combustion	...	....	....	9.91	9.16	9.96	....	9.98
C in residue	....	....	....	2.65	2.03	....	....	2.30
Total carbon	....	....	....	12.56	11.19	....	....	12.28

WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VA., June, 1896.

DIPYRIDINE METHYLENE IODIDE AND THE NON-FORMATION OF THE CORRESPONDING MONOPYRIDINE PRODUCTS.[1]

BY S. H. BAER and A. B. PRESCOTT.

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THE addition compound of pyridine and methylene iodide was formed in different ways, varying the conditions of mass, temperature, pressure, and time, as follows. The method of preparation recommended is that of No. V.

Preparation I.—Pyridine and methylene iodode in equimolecular proportions, reacting at laboratory temperature, for two days, form a dark-red crystalline mass. This was washed in cold alcohol, which does not dissolve it.

Preparations II and III.—The same proportions (those of a monopyridine product) were taken in reaction at 120° C. The methyl iodide for I and II was colored with free iodine, that for III was obtained colorless by distillation in vacuum. In each case the crystals, washed with cold alcohol, were dark-red. This color was not affected by treating the crystals with thiosulphate solution, and therefore not due to free iodine or to periodides.

Preparation IV.—By reaction of colorless methylene iodide, in the same proportions, with the pyridine, but without heat, an orange precipitate settles slowly. This was washed as the others.

Preparation V.—Pyridine of boiling point 118° C., and methylene iodide either colorless or tinged with iodine, in about equal molecular quantities, are placed in a flask, alcohol in volume equal to the two reacting materials is added, a return-condenser adjusted, and the heat of a water-bath applied for an hour. On cooling, long yellow needles separate out. To purify further, dissolve in hot fifty per cent. alcohol, cool, and add a little ether, when fine crystals are formed.

So obtained, the product is in fine needles, of yellow color, decomposing, not melting, at 220° C.; soluble in water, from which it crystallizes at 0° C.; insoluble in cold alcohol, sparingly soluble in hot alcohol; insoluble in ether, or chloroform, or benzene, or amyl alcohol; sparingly soluble in methyl alcohol.

Analysis gave us percentages as follows:

	Calculated for $(C_5H_5N)_2CH_2I_2$.	Found.				
		I.	II.	III.	IV.	V.
I	59.61	58.95	58.91	57.98	58.4	59.6
N........	6.57	....	....	....	...	6.72

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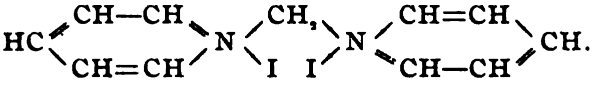
[1] Read at the Buffalo meeting of the American Association for the Advancement of Science.

The product, therefore, not quite pure in the first four experimental preparations, is substantially the same under the different conditions employed, and with whatever excess of the diiodomethane, is always the dipyridine addition compound. And its formula, agreeing with those of its bromine homologues,[1] may be confidently written, to express the relations of the methylene group and the halogen atoms:



Kleine found[2] that trimethylamine, in combination with dihalogen substituted hydrocarbons, forms both the monammonium and the diammonium products, the former prevailing, especially when there are not more than two atoms of carbon in the halide.

It seemed now desirable to subject pyridine to various conditions of additive reaction with various dihalides, in order to know whether it can in any case form such monamine compounds as the fatty amines sometimes form.[3] Pyridine and ethylene bromide, in equal molecular proportions, were digested together in a sealed tube for two weeks, when the entire content, a crystalline mass, was dissolved in hot alcohol of ninety-five per cent., and fractionally crystallized in successive crops, washing each with cold absolute alcohol. These crops of crystals gave, of bromine, respectively, 46.15, 46.15, 46.18, and 46.03 per cent., the calculated per cent. in $(C_5H_5N)_2C_2H_4Br_2$ being 46.21.

Next pyridine with excess of ethylene bromide was digested in a pressure flask, in water-bath, with agitation. The crystallized product gave 46.26 per cent. of bromine. Finally dipyridine ethylene bromide was heated with excess of ethylene bromide in a sealed tube to 170° C. There was some charring in the mixture. By recrystallizing from it a product was obtained which gave 45.84 per cent. of bromine.

Dipyridine ethylene bromide crystallizes in colorless plates, insoluble in ether, and melting with decomposition at 295° C.

UNIVERSITY OF MICHIGAN.

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[1] The ethylene bromide, (Hofmann) Davidson, 1861: *Proc. Roy. Soc.*, page 261; The trimethylene bromide, Flintermann and Prescott, 1895: *J. Am. Chem. Soc.*, **18**, 28.

[2] G. Kleine, 1894: *Chem. Centrbl.*, page 161.

[3] This in continuation of the inquiry of Flintermann and Prescott; 1895: *J. Am. Chem. Soc.*, **18**, 33.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.
No. 13.]

DETERMINATION OF THE ATOMIC MASSES OF SILVER, MERCURY AND CADMIUM BY THE ELECTROLYTIC METHOD.[1]

BY WILLETT LEPLEY HARDIN.

Received September 26, 1896.

INTRODUCTION.

A glance at the literature on the determinations of the atomic masses of silver, cadmium and mercury will show that, with the exception of cadmium, the electrolytic method has not been tried. Aside from the fact that certain errors involved in the washing and drying of the precipitates are eliminated by this method, its simplicity at once gives it preference over the usual methods of gravimetric determinations. Inasmuch as these three metals are completely precipitated from certain of their solutions by the electric current, and as it is desirable to determine the atomic mass of any element by different methods, it was thought advisable to apply this method in a redetermination of the atomic masses of these elements.

GENERAL CONSIDERATIONS.

Before taking up the different metals separately, the following general considerations may be mentioned :

1. A careful preliminary study was made in the selection of compounds. Some compounds, which from a theoretical standpoint seemed to offer certain advantages, were found by experiment not to meet the requirements of exact determinations. Salts which can be sublimed were used whenever possible ; and in all cases only those salts were used which form well defined crystals.

2. All reagents used were either prepared or purified by myself and carefully tested for impurities.

3. The metals were deposited in platinum dishes of about 200 cc. capacity and about sixty-five grams in weight. When the precipitation was complete, before interrupting the current, the

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[1] From the author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Ph.D., 1896.

solution was siphoned from the platinum dish, pure water being added at the same time; this was continued until the solvent used was completely removed from the dish. The current was then interrupted and the deposit washed several times with boiling water, with the hope of removing any occluded hydrogen. After drying, the dishes were placed in a vacuum desiccator over anhydrous calcium chloride and allowed to remain in the balance room until their temperature was the same as that of the room. Atmospheric dust was excluded from the platinum dishes during the process of deposition by means of two glass plates which formed a complete cover; the moisture which collected on this cover was washed back into the dish from time to time. The dishes were handled with nickel tongs tipped with rubber.

4. The balance used was made expressly for this work by Henry Troemner, of Philadelphia. The beam and pans were made of aluminum, the beam being about twenty centimeters long. The framework was plated with gold to prevent corrosion. The sensibility for different loads and the ratio of the length of the two arms were carefully determined. The balance is sensitive to the fortieth of a milligram, and the sensibility is almost independent of the load up to seventy-five grams. The difference in the length of the two arms is so slight that no correction need be applied. The balance was kept in a large quiet room of nearly constant temperature.

The larger weights used were made of brass and the fractions of a gram made of platinum. The weights were all previously compared against each other and standardized with reference to the largest weight. The small corrections found in comparing them were tabulated and applied to all results. The weighings were made by the method of oscillations. The temperature and barometic pressure were noted at the time of each weighing, and all weighings were reduced to a vacuum standard. As the density of the atmosphere at the time of weighing the empty platinum dish was different from that at the time of weighing the dish and deposit together, the following formula was applied to obtain the weight of the deposit *in vacuo*:

$$\left[\text{Weight of (dish} + \text{deposit)} - \frac{\text{weight of dish}\left(1 + \frac{\lambda}{\Delta} - \frac{\lambda}{\delta}\right)}{1 + \frac{\lambda'}{\Delta} - \frac{\lambda'}{\delta}}\right] \times \left[1 + \frac{\lambda'}{\Delta'} - \frac{\lambda'}{\delta}\right] = \text{weight of deposit } \textit{in vacuo}.$$

Where λ = density of air at the time of weighing the empty dish.

λ' = density of air at the time of weighing the dish + deposit.

Δ = density of platinum dish.

Δ' = density of metallic deposit.

δ = density of weights.

As the weights were all standardized with reference to the hundred-gram brass weight, it is evident that they must all be calculated as having the same density, equal to that of brass.

5. The atomic masses of the different elements involved in the calculation of results were taken from Clarke's latest report.[1]

PART I.

DETERMINATION OF THE ATOMIC MASS OF SILVER.

The mean of all the earlier determinations, as calculated by Clarke, gives 107.923 for the atomic mass of silver; a result almost identical with the mean (107.93; O = 16) of the determinations of Stas.

PREPARATION OF PURE METALLIC SILVER.

The silver used in this work was purified by the Stas method. Two hundred grams of silver, about ninety-nine per cent. pure, were dissolved in dilute hot nitric acid. The solution was evaporated to dryness, the nitrate heated to fusion and maintained in a fused condition until the oxides of nitrogen were no longer evolved. The residue, after cooling, was dissolved in as little cold water as possible, and after standing forty-eight hours the solution was filtered through a double filter to remove any suspended matter. The clear solution was then diluted with thirty times its volume of distilled water, and to it was added an

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[1] *J. Am. Chem. Soc.*, **18**, 197.

excess of pure hydrochloric acid. The silver chloride which separated was allowed to subside and was then thoroughly washed by decantation, at first with water containing a little hydrochloric acid, and finally with pure water. The precipitate was then collected on a cheese cloth filter, pressed strongly and allowed to dry. When perfectly dry, the silver chloride was powdered finely and digested for three days with aqua regia; it was then thoroughly washed by decantation with distilled water. After obtaining the pure chloride of silver, it was necessary to purify the caustic potash and milk sugar used in reducing the chloride to the metallic state. The caustic potash was heated to the boiling point and to it was added a concentrated solution of potassium sulphide to precipitate any heavy metals which might be present. The solution was filtered and the filtrate digested for some time with freshly precipitated silver oxide and again filtered to remove the excess of potassium sulphide. The milk sugar was purified in a similar manner. The silver chloride was then placed in large porcelain dishes and covered with a solution of caustic potash and milk sugar. The dishes were placed on a water-bath and heated to a temperature of 70°–80° until the reduction to finely divided metallic silver was complete. The alkaline solution was then poured off, and the gray metallic silver was washed with distilled water until the alkaline reaction disappeared. The metal was then digested with pure dilute sulphuric acid, and finally washed with dilute ammonia water. The silver thus obtained was mixed, when dry, with five per cent. of its weight of fused borax containing ten per cent. of pure sodium nitrate. The mixture was fused in a clay crucible and the silver poured into a mold. The metal obtained in this way was almost snow white in appearance, and dissolved completely in nitric acid to a colorless solution.

PREPARATION OF PURE NITRIC ACID.

To obtain pure nitric acid, one-half liter of the commercial C. P. acid was mixed with an equal volume of concentrated C. P. sulphuric acid and distilled from a retort provided with a knee tube and condenser. The first portion of the distillate was rejected. The process was stopped when half of the nitric acid present had been distilled over. The distillate was mixed with an equal volume of pure sulphuric acid and redistilled. The second distillate was collected in a flask, the mouth of which was closed with glass wool. When the process was complete, the flask was closed with a doubly perforated cork and placed in a water-bath at a temperature of 40°. A current of pure dry air was then conducted through the acid to remove any oxides of nitrogen. The acid was kept in a dark place.

EXPERIMENTS ON SILVER OXIDE.

If pure, dry silver oxide could be prepared, the atomic mass of silver could be compared directly with that of oxygen. A large number of experiments were made on this compound with the hope of determining the ratio of the atomic masses of these two elements.

PREPARATION OF SILVER OXIDE.

A portion of the pure metallic silver was dissolved in pure dilute nitric acid and the solution evaporated to crystallization. The crystals of silver nitrate were dissolved in pure water and to the solution was added a solution of pure sodium hydroxide, prepared by throwing pieces of metallic sodium on distilled water in a platinum dish. The twenty-five grams of silver oxide prepared in this way were washed by decantation with twenty liters of water. The material was then dried at the ordinary temperature, after which it was finely powdered and dried for twenty-four hours in an air-bath at 100°. The oxide was kept in a weighing tube in a dark place.

Several analyses were made by dissolving a weighed portion of the material in pure potassium cyanide, electrolyzing the solution and weighing the resulting metallic silver. The observations invariably gave less than ninety-five for the atomic mass of silver. The oxide was redried at a temperature of 125° and analyzed as before, but the quantity of silver obtained was far below that calculated for the compound Ag_2O. Observations were also made on material dried at 140° and 150°. The results showed that it was impossible to prepare the silver oxide in a pure, dry condition.

After making these observations, my attention was called to an article by M. Carey Lea,[1] in which were given the results of a series of analyses of silver oxide dried at different temperatures varying from 100° to 170°. These observations prove conclusively that oxygen is given off at a much lower temperature than that required to remove the last traces of moisture. From these observations and the results obtained by myself, it was evident that any further attempt to determine the atomic mass of silver from the oxide would be useless.

Although no careful study was made as to the nature of this compound, it might be added that, from my own observations, it seems very probable that the oxide contains some hydrogen in the form of hydroxyl.

FIRST SERIES.

EXPERIMENTS ON SILVER NITRATE.

The nitrate of silver seems to fulfil the conditions necessary for accurate analyses, inasmuch as it is stable and crystallizes in well defined crystals which can be fused without decomposition.

PREPARATION OF SILVER NITRATE.

The material used in these experiments was prepared by dissolving pure silver in pure aqueous nitric acid in a porcelain dish. An excess of silver was used, and after complete saturation the solution was poured off from the metal into a second dish and evaporated to crystallization. The perfectly transparent, rhombic plates of silver nitrate which separated were dissolved in pure water and recrystallized. The crystals were then carefully dried, placed in a platinum crucible which rested in a larger platinum dish and gradually heated to fusion. After cooling, the perfectly white opaque mass was broken up and placed in a ground-glass stoppered weighing tube and kept in a desiccator in a dark place.

MODE OF PROCEDURE.

The platinum dish in which the deposit was made was care-

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[1] *Am. J. Sci.*, 44, 240.

fully cleaned with nitric acid and dried to constant weight. It was then placed in a desiccator over anhydrous calcium chloride, and this, together with the desiccator containing the tube of silver nitrate, was placed in the balance room, where they were allowed to remain until their temperatures were the same as that of the room. After weighing the platinum dish, the tube of silver nitrate was weighed and part of the salt removed to the dish, after which the tube was reweighed. The difference in the two weighings, of course, represented the weight of silver nitrate used in the experiment. Enough water to dissolve the nitrate was added to the dish, and then a solution of potassium cyanide, made by dissolving seventy-five grams of pure potassium cyanide in one liter of water, was added until the silver cyanide first formed was completely dissolved. The dish was then filled to within a quarter of an inch of the top with pure water and the solution electrolyzed with a gradually increasing strength of current. The following table will show the strength of current and the time through which it acted :

Time of action.	Strength of current.
2 hours	$N.D_{100} = 0.015$ amperes.
4 "	$N.D_{100} = 0.030$ "
6 "	$N.D_{100} = 0.075$ "
4 "	$N.D_{100} = 0.150$ "
4 "	$N.D_{100} = 0.400$ "

By gradually increasing the strength of current in this way the silver came down in a dense, white deposit. When the deposition was complete, before interrupting the current, the liquid was siphoned from the dish, pure water being added at the same time. This was continued until the cyanide was completely removed. The dish with the deposit was washed several times with boiling water and carefully dried. It was then placed in a desiccator and allowed to remain in the balance room until its temperature was the same as that of the room, when it was reweighed.

Weight of platinum dish = 71.27302 grams.

Weight of silver nitrate = 0.31198 grams.

Temperature, 22°.

Barometric pressure, 770 mm.

Weight of platinum dish + silver deposit = 71.47104 grams.

Temperature, 22°.

Barometric pressure, 760 mm.

Density of silver nitrate = 4.328.

" " brass weights = 8.5.

" " platinum dish = 21.4.

" " metallic silver = 10.5.

" " atmosphere at the time of weighing the empty dish and silver nitrate = 0.001212.

" " atmosphere at the time of weighing the platinum dish + silver deposit = 0.001196.

Computing on this basis we have the following:

$$0.31198\left(1+\frac{0.001212}{4.328}-\frac{0.001212}{8.5}\right) = 0.31202$$ = weight of $AgNO_3$ *in vacuo.*

$$71.27302\left[\frac{1+\frac{0.001212}{21.4}-\frac{0.001212}{8.5}}{1+\frac{0.001196}{21.4}-\frac{0.001196}{8.5}}\right] = 71.27291$$ = weight of platinum dish at 22° and 760 mm.

$71.47104 - 71.27291 = 0.19813$ = weight of deposit at 22° and 760 mm.

$$0.19813\left(1+\frac{0.001196}{10.5}-\frac{0.001196}{8.5}\right) = 0.19812$$ = weight of deposit *in vacuo.*

Taking $O = 16$ and $N = 14.04$, the atomic mass of silver =

$$\frac{0.19812 \times 62.04}{(31202 - 19812)} = 107.914.$$

Ten observations on silver nitrate computed in the foregoing manner are as follows:

	Weight of $AgNO_3$. Gram.	Weight of Ag. Gram.	Atomic mass of silver.
1	0.31202	0.19812	107.914
2	0.47832	0.30370	107.900
3	0.56742	0.36030	107.923
4	0.57728	0.36655	107.914
5	0.69409	0.44075	107.935
6	0.86367	0.54843	107.932
7	0.86811	0.55130	107.960

	Weight of $AgNO_3$. Gram.	Weight of Ag. Gram.	Atomic mass of silver.
8.	0.93716	0.59508	107.924
9	1.06170	0.67412	107.907
10	1.19849	0.76104	107.932

Mean = 107.924
Maximum = 107.960
Minimum = 107.900

Difference = 0.060
Probable error = ±0.005

Computing the atomic mass of silver from the total quantity of material used and metal obtained, we have 107.926.

SECOND SERIES.

EXPERIMENTS ON SILVER ACETATE.

The fact that silver forms well crystallized salts with a number of organic acids makes the comparison of the atomic mass of silver with the combined atomic masses of carbon, hydrogen, and oxygen, a matter of no great difficulty. From certain preliminary experiments, the acetate of silver seemed to fulfill the conditions necessary for accurate determinations.

PREPARATION OF SILVER ACETATE.

The purest commercial sodium acetate was dissolved in water, the solution filtered and recrystallized. After three crystallizations the material was dissolved in pure water, and to the rather concentrated solution was added a solution of silver nitrate, prepared in the manner already indicated. The white curdy precipitate which separated, after washing with cold water, was dissolved in hot water, the solution filtered and evaporated to crystallization. The silver acetate separated in brilliant sword-shaped crystals. After pouring off the solution the crystals were quickly rinsed with cold water and placed between filters to remove the adhering moisture. The material was allowed to remain in contact with the filters only for a short time. It was then placed in a platinum dish, and when apparently dry the crystals were broken up into a finely divided condition and dried forty-eight hours in a vacuum desiccator. This work was carried on in a darkened room, and the silver acetate obtained was placed in a weighing tube, and kept in a desiccator in a dark place.

MODE OF PROCEDURE.

The method of operation was similar to that described under silver nitrate. After weighing the silver acetate, its aqueous or cyanide solution was electrolyzed and the weight of the resulting metallic silver determined. The results obtained from the aqueous solution were sometimes vitiated by the separation of silver peroxide at the anode. To prevent this, potassium cyanide was sometimes added. The results, however, from the two solutions were practically the same when no peroxide separated. From the aqueous solution the silver was deposited in a crystalline form. The strength of current and time of action were the same as for silver nitrate.

Ten observations on silver acetate reduced to a vacuum standard on the basis of

3.241 = density of silver acetate,
10.5 = " metallic silver,
24.4 = " platinum dish,
8.5 = " weights,

and computed for the formula $AgC_2H_3O_2$, assuming the atomic masses of carbon, hydrogen and oxygen to be 12.01, 1.008 and 16, respectively, are as follows:

	Weight of $AgC_2H_3O_2$. Grams.	Weight of Ag. Gram.	Atomic mass of silver.
1	0.32470	0.20987	107.904
2	0.40566	0.26223	107.949
3	0.52736	0.34086	107.913
4	0.60300	0.38976	107.921
5	0.67235	0.43455	107.896
6	0.72452	0.46830	107.916
7	0.78232	0.50563	107.898
8	0.79804	0.51590	107.963
9	0.92101	0.59532	107.925
10	1.02495	0.66250	107.923

Mean = 107.922
Maximum = 107.963
Minimum = 107.896

Difference = 0.067
Probable error = ± 0.005

Computing from the total quantity of material used and metal obtained we have 107.918 for the atomic mass of silver.

EXPERIMENTS ON SILVER SUCCINATE.

Silver succinate was prepared in a manner similar to that of silver acetate. The commercial C. P. succinic acid was recrystallized three times; the ammonium salt was then prepared and its aqueous solution precipitated with a solution of pure silver nitrates. The precipitate of silver succinate was thoroughly washed by decantation with pure water and carefully dried. After drying for several hours in an air-bath at 50°, the material was ground in an agate mortar to a finely divided powder, and was then redried for twenty-four hours in an air-bath at a temperature of 60°. The white powder obtained in this way was placed in a weighing tube and kept in a desiccator.

The method of analysis was similar to that of silver acetate. A weighed portion of the material was dissolved in a little potassium cyanide in a platinum dish. After diluting with pure water, the solution was electrolyzed and the resulting deposit weighed. The strength of current and time of action were the same as for silver nitrate. The results computed for the formula $C_4H_4O_4Ag_2$ were not constant, and were invariably from one to two units lower than those obtained from silver nitrate and silver acetate. The material was then dried at a temperature of 75°, but the results obtained were not satisfactory.

The two most probable causes for these low results are:

First, the difficulty of removing the last traces of impurities from a precipitate like that of silver succinate. The experience throughout this work has been, that, to remove all the impurities from a finely divided precipitate by washing is almost impossible.

Second, the difficulty met in drying material of this kind. This same difficulty was met in the experiments on silver oxide which, as shown by Lea, retained moisture up to 165°.

THIRD SERIES.

EXPERIMENTS ON SILVER BENZOATE.

The preceding work on silver acetate and silver succinate shows the necessity of selecting compounds which form well defined crystals. Perhaps no organic salt of silver fulfils the conditions necessary for accurate analyses better than silver benzoate.

PREPARATION OF SILVER BENZOATE.

The purest commercial benzoic acid was resublimed three times from a porcelain dish into a glass beaker. The product thus obtained was dissolved in pure aqueous ammonia and the solution evaporated to crystallization. The ammonium salt was then dissolved in distilled water and to the solution was added a solution of pure silver nitrate. The white precipitate of silver benzoate which separated was washed with cold water; it was then dissolved in hot water, the solution filtered, and evaporated to crystallization. The salt separated in fine needles, which clung together in arborescent masses. After removing the liquid from the beaker, the crystals were quickly rinsed with cold water and placed between filters to remove the adhering moisture. When apparently dry they were broken up into small fragments and dried forty-eight hours in a vacuum desiccator. The material was then placed in a glass stoppered weighing tube and kept in a dark place.

MODE OF PROCEDURE.

The details of the method of operation are the same as those given under silver nitrate. A weighed portion of the material was dissolved in a dilute solution of potassium cyanide in a platinum dish. The solution was then electrolyzed and the resulting metal weighed. The strength of current and time of action were the same as for silver nitrate.

Before the results could be reduced to a vacuum standard it was necessary to determine the specific gravity of silver benzoate. This was done by means of a specific gravity bottle, the liquid used being chloroform. The mean of two determinations gave 2.082 for the specific gravity of silver benzoate.

Ten results on this compound, reduced to a vacuum standard on the basis of

2.082 = density of silver benzoate,
10.5 = " " metallic silver,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $C_7H_5AgO_2$, assuming 12.01, 1.008, and 16 to be the atomic masses of carbon, hydrogen and oxygen, respectively, are as follows :

	Weight of $C_7H_5AgO_2$. Grams.	Weight of Ag. Gram.	Atomic mass of silver.
1	0.40858	0.19255	107.947
2	0.46674	0.21999	107.976
3	0.48419	0.22815	107.918
4	0.62432	0.29418	107.918
5	0.66496	0.31340	107.964
6	0.75853	0.35745	107.935
7	0.76918	0.36247	107.936
8	0.81254	0.38286	107.914
9	0.95673	0.45079	107.908
10	1.00840	0.47526	107.962

Mean = 107.938
Maximum = 107.976
Minimum = 107.908

Difference = 0.068
Probable error = ±0.005

Computing from the total quantity of material used and metal obtained we have 107.936 for the atomic mass of silver.

SUMMARY.

In discussing the work on the atomic mass of silver, two possible sources of error suggest themselves.

First, the hydrogen which is continually being set free in the process of electrolysis may, in part, be occluded by the metallic silver. As already pointed out, the metallic deposits were washed several times with boiling water, with the hope of removing any occluded gases ; but whether this effected a complete removal of all the occluded gases was not determined.

Second, the condensation of moisture on the platinum dish might be urged as a possible source of error. But it must be remembered that the dish was dried in the same manner each time and kept for several hours in a desiccator, and that the atmosphere inside the balance was kept dry by means of several beakers of anhydrous calcium chloride, and that the temperature of the balance room throughout the work was almost constant. Under these conditions there is but little chance of error from different amounts of moisture condensed. Moreover, the variation in the different weighings of the same dish was very slight.

The advantages of the method are evident.

First, the great advantage of the method is its extreme simplicity.

Second, the nature of the compounds used and of metallic silver renders them well adapted to weighing.

Third, the method was such as to eliminate the errors incident to the ordinary gravimetric methods of analysis.

Of the three series, the first is probably entitled to the greatest weight. That the silver nitrate was pure and free from moisture seems beyond question. However, the close agreement of the last two series with the first indicates that the acetate and benzoate of silver were also free from moisture.

Giving equal weight to each of the three series, we have the following as the general mean computed from the separate observation :

	Atomic mass of silver.
First series	107.924
Second "	107.922
Third "	107.938
General mean =	107.928

Computing the general mean from the total quantities of material used and metal obtained we have :

	Atomic mass of silver.
First series	107.926
Second "	107.918
Third "	107.936
General mean =	107.927

Combining this with the first general mean we have 107.9275 as the final result for the atomic mass of silver.

PART II.

DETERMINATION OF THE ATOMIC MASS OF MERCURY.

From all the earlier determinations Clarke gives 200 as the most probable value for the atomic mass of mercury, assuming oxygen equal to 16.

EXPERIMENTS ON MERCURIC OXIDE.

A large number of experiments were made with a view of determining the ratio of mercury to oxygen in mercuric oxide. The method proved to be unsatisfactory, although, apparently very good results were obtained in some preliminary experiments. The cause of this close agreement of results will be explained in the details of the work.

PREPARATION OF PURE MERCURIC OXIDE.

The purest commercial mercuric chloride was carefully sublimed from a porcelain dish into a glass funnel. The sublimed portion was dissolved in water, the solution filtered, and evaporated to crystallization. The crystals were then thoroughly dried and carefully resublimed. The product obtained in this way consisted of white crystalline leaflets which dissolved completely in water. Pure sodium hydroxide was then prepared by throwing pieces of metallic sodium on pure water contained in a platinum dish. To the pure sodium hydroxide was added a solution of mercuric chloride, the former always being in excess. The yellow mercuric oxide which separated was washed for several days by decantation with hot water. The material was then dried twenty-four hours in an air-bath at 105°.

MODE OF PROCEDURE.

In a series of preliminary experiments made in the spring of 1895, a weighed portion of mercuric oxide prepared in the above manner was dissolved in a dilute solution of potassium cyanide in a platinum dish. The solution was then electrolyzed and the weight of the resulting metallic mercury determined. Inasmuch as the results obtained in these preliminary experiments were not reduced to a vacuum standard, it was thought advisable to weigh the empty platinum dish after removing the metallic deposit in order that the two weighings might be made under approximately the same conditions. The results for the most part agreed very closely and differed very little from the results obtained by other methods. Six observations computed for the formula HgO, assuming the atomic mass of oxygen to be 16, are as follows:

	Weight of HgO. Gram.	Weight of Hg. Gram.	Atomic mass of mercury.
1	0.26223	0.24281	200.05
2	0.23830	0.22065	200.02
3	0.23200	0.21482	200.06
4	0.14148	0.13100	200.00
5	0.29799	0.27592	200.03
6	0.19631	0.18177	200.02

Mean = 200.03.

These results were selected from a larger series. After making the above observations it was noticed that the platinum dish had gradually decreased in weight throughout the work. This decrease in weight indicated that the mercury deposit had formed an amalgam with the platinum dish, which was soluble in hot nitric acid. To ascertain whether such was the case or not the platinum dish, after weighing, was filled with a solution of the double cyanide of mercury and potassium and the solution electrolyzed. On dissolving the mercury deposit in cold nitric acid a dark colored film remained on the sides of the dish. The dish was then carefully washed, dried and reweighed, and found to be heavier than at the beginning of the operation, showing that the mercury had not been completely removed. The dark film was then dissolved in hot nitric acid and the dish again weighed. This last weight being less than that at the beginning showed that some of the platinum had been dissolved from the dish. The nitric acid solution of the dark film was evaporated to dryness and ignited to remove the mercury. The residue was dissolved in aqua regia, the solution evaporated to dryness, and enough water added to dissolve the small residue. A little concentrated ammonium chloride was then added to the solution, and the double chloride of ammonium and platinum separated as a yellow crystalline powder. This proved conclusively that the mercury deposit had united with the platinum dish to form an amalgam which was soluble in hot nitric acid. Hence the results given for mercuric oxide are of no value in determining the atomic mass of mercury.

A series of careful experiments was then made on the oxide dried at different temperatures. To avoid any error from the amalgam which formed with each deposit, the platinum dish was weighed at the beginning of each observation, the temperature and barometric pressure being noted at the same time. The results obtained from the oxide dried at a temperature of 105° gave from 180 to 185 for the atomic mass of mercury. The material was then dried at a temperature of 125°, but the increase in the amount of mercury obtained was very slight. Finally with material dried at 150°, the results obtained for the atomic mass of mercury were all below 195°.

The most probable causes for these low results are:

First, the difficulty of removing the last traces of alkalies from the mercuric oxide.

Second, the difficulty met in the complete removal of the moisture from an amorphous precipitate. This difficulty as well as the first was referred to in the experiments on silver oxide.

Third, mercuric oxide does not form a clear solution with potassium cyanide. There seems to be a slight reduction of the oxide to the metallic state. It is difficult to determine whether this reduced portion unites completely with the metallic deposit or is partially removed in the process of washing. The latter is probably true, and it may be that a different method of analysis would give more accurate results for this compound.

FIRST SERIES.

EXPERIMENTS ON MERCURIC CHLORIDE.

The material used in this series of experiments was prepared from the commercial C. P. mercuric chloride. The product was first dissolved in water, the solution filtered and evaporated to crystallization. The crystals were dried and carefully sublimed from a porcelain dish into a glass funnel. The sublimed portion was dissolved in water, the solution filtered and evaporated to crystallization. These crystals were dried as before and carefully resublimed. The material was then placed in a weighing tube and kept in a desiccator.

MODE OF PROCEDURE.

The method of operation was similar to that already described under the different compounds of silver. A weighed portion of the mercuric chloride was dissolved in a little potassium cyanide and the solution electrolyzed. The deposit was washed and dried and handled in every way like the deposits of silver. The strength of the current and time of action were as follows:

Time of action.	Strength of current.
4 hours	$N.D_{100} = 0.02$ amperes.
6 "	$N.D_{100} = 0.05$ "
6 "	$N.D_{100} = 0.10$ "
6 "	$N.D_{100} = 0.30$ "

A current of gradually increasing strength deposits the mercury in extremely small globules, which can be washed and handled more easily than the larger globules obtained by using a strong current at first. In cases where more than one-half gram of metal was deposited the strong current was allowed to act two hours longer.

Ten results on mercuric chloride reduced to a vacuum standard on the basis of

5.41 = density of mercuric chloride,
13.59 = " " metallic mercury,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed from the formula $HgCl_2$, assuming 35.45 to be the atomic mass of chlorine, are as follows:

	Weight of $HgCl_2$. Grams.	Weight of Hg. Grams.	Atomic mass of mercury.
1	0.45932	0.33912	200.030
2	0.54735	0.40415	200.099
3	0.56002	0.41348	200.053
4	0.63586	0.46941	199.947
5	0.64365	0.47521	200.026
6	0.73281	0.54101	199.988
7	0.86467	0.63840	200.838
8	1.06776	0.78825	199.946
9	1.07945	0.79685	199.917
10	1.51402	1.11780	200.028

Mean = 200.006
Maximum = 200.099
Minimum = 199.917

Difference = 0.182
Probable error = ±0.011

Computing from the total quantity of material used and metal obtained we have 199.996 for the atomic mass of mercury.

SECOND SERIES.

EXPERIMENTS ON MERCURIC BROMIDE.

The bromine used in these experiments was prepared by distilling the commercial C. P. bromine twice over manganese dioxide. Any trace of chlorine which might be present would be removed by this method.

PREPARATION OF MERCURIC BROMIDE.

Fifty grams of metallic mercury were placed in a beaker and covered with water. Pure bromine was then added until the mercury was completely saturated. The contents of the beaker were then digested with hot water until the mercuric bromide dissolved; the solution was filtered and evaporated to crystallization. The white crystals of mercuric bromide which separated were thoroughly dried and carefully sublimed from a porcelain dish into a glass funnel. Only the middle portion of the sublimate was used in the experiments. The product obtained in this way consisted of brilliant crystalline leaflets which dissolved completely in water. The material was kept in a weighing tube in a desiccator.

MODE OF PROCEDURE.

The method of analysis was exactly like that described under mercuric chloride. A weighed portion of the mercuric bromide was dissolved in dilute potassium cyanide in a platinum dish. The solution was then electrolyzed and the resulting metal weighed. The strength of current and time of action were the same as for mercuric chloride.

Ten results on mercuric bromide reduced to a vacuum standard on the basis of

5.92 = density of mercuric bromide,
13.59 = " " metallic mercury,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $HgBr_2$, assuming 79.95 to be the atomic mass of bromine, are as follows :

	Weight of $HgBr_2$. Grams.	Weight of Hg. Grams.	Atomic mass of mercury.
1	0.70002	0.38892	199.898
2	0.56430	0.31350	199.876
3	0.57142	0.31750	199.938
4	0.77285	0.42932	199.832
5	0.80930	0.44955	199.814
6	0.85342	0.47416	199.911
7	1.11076	0.61708	199.869
8	1.17270	0.65145	199.840
9	1.26186	0.70107	199.899
10	1.40142	0.77870	199.952

Mean = 199.883
Maximum = 199.952
Minimum = 199.814

Difference = 0.138
Probable error = ±0.010

Computing from the total quantity of material used and metal obtained, the atomic mass of mercury is 199.885.

THIRD SERIES.

EXPERIMENTS ON MERCURIC CYANIDE.

A series of observations was made on several organic salts of mercury with a view of selecting a compound suitable for atomic mass determinations. Mercuric acetate and other similar salts were found to be unstable in the air and unsuited for accurate analyses. Mercuric cyanide, on the other hand, was found to be perfectly stable and to form well defined crystals.

PREPARATION OF HYDROCYANIC ACID.

Five hundred grams of potassium ferrocyanide were placed in a two liter retort connected with a condenser. A cooled mixture of 300 grams of pure sulphuric acid and 700 cc. of distilled water was then poured into the retort and the mixture carefully heated until the hydrocyanic acid was distilled over into the receiver. The product obtained was redistilled and used immediately in the preparation of mercuric cyanide.

PREPARATION OF MERCURIC CYANIDE.

Fifty grams of mercuric oxide, prepared as already described in the experiments on mercuric oxide, were dissolved in pure, warm hydrocyanic acid. The solution was then filtered and evaporated to crystallization. The transparent crystals of mercuric cyanide which separated were dissolved in pure water and recrystallized. The product obtained by the second crystallization was quickly rinsed with cold water and dried for six hours in an air bath at a temperature of 50°. The crystals were then ground to a finely divided powder in an agate mortar and redried for twenty-four hours in an air bath at a temperature of 55°. The dry, white powder was then placed in a weighing tube and kept in a desiccator.

MODE OF PROCEDURE.

The mode of procedure with mercuric cyanide was somewhat different from that of the preceding experiments, in that no potassium cyanide was used in preparing the solution for electrolysis. A weighed portion of the material was dissolved in pure water in a platinum dish. When the crystals had completely dissolved, the dish was filled to within a quarter of an inch of the top with water, after which one drop of pure sulphuric acid was added. The solution was then electrolyzed and the resulting metal weighed. The strength of the current and the time of action were the same as for mercuric chloride. In the last four experiments, where rather large quantities of mercury were deposited, the strong current was allowed to act from two to six hours longer.

The results of ten experiments on mercuric cyanide, reduced to a vacuum standard on the basis of

4.0 = density of mercuric cyanide,
13.59 = " " metallic mercury,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $Hg(CN)_2$, assuming 12.01 and 14.04 to be the atomic masses of carbon and nitrogen, respectively, are as follows :

	Weight of $Hg(CN)_2$. Grams.	Weight of Hg. Grams.	Atomic mass of mercury.
1	0.55776	0.44252	200.063
2	0.63290	0.50215	200.092
3	0.70652	0.56053	200.038
4	0.80241	0.63663	200.075
5	0.65706	0.52130	200.057
6	0.81678	0.64805	200.103
7	1.07628	0.85392	200.077
8	1.22615	0.97282	200.071
9	1.66225	1.31880	200.057
10	2.11170	1.67541	200.077

Mean = 200.071
Maximum = 200.103
Minimum = 200.038

Difference = 0.065
Probable error = 0.005

From the total quantity of material used and metal obtained, the atomic mass of mercury is 200.070.

FOURTH SERIES.

According to Faraday's law the quantities of different metals deposited from their solutions by the same current are proportional to their equivalent weights. In this series of experiments an attempt was made to determine the ratio of the atomic mass of mercury to that of silver by passing the same current through the solutions of the two metals and weighing the two resulting deposits. If the proper conditions could be obtained, this would certainly be the simplest and most direct method for comparing the equivalent weights of different metals. But so many difficulties were met that the method on the whole was not satisfactory.

In the "Revision of the Atomic Weight of Gold,"[1] Mallet made use of this method, and in a series of careful preliminary experiments determined the conditions most favorable to its application. From a number of experiments made by passing the same current through two different solutions of copper sul-

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[1] *Am. Chem. J.*, 12, 182.

phate, using pure electrotype copper for both anode and cathode in each solution, Mallet found:

First.—Other conditions being the same, the difference in the quantities of metal deposited from solutions of unequal concentrations was very slight and somewhat variable, but the tendency was toward a slightly larger quantity from the more concentrated solution.

Second.—With equal quantities of metal in the two solutions and unequal quantities of free acid, the difference in the results obtained were almost insignificant and somewhat variable in direction, the tendency being toward a slightly larger quantity from the less acid solution.

Third.—Other conditions being the same, a difference in the temperature of the two solutions invariably caused a slightly larger deposit from the cooler solution.

Fourth.—Other conditions being the same, a difference in the size of the copper plates, and hence a difference in the "current density," caused a slightly greater deposit on the smaller plate.

Fifth.—A difference in the distance between the two plates did not produce a constant difference of result, but the tendency was toward a slightly larger deposit on the cathode plate farther separated from its anode.

From the foregoing experiments it is evident that the conditions most favorable to this method are, that the two solutions should be equally concentrated, of the same temperature, and should contain equal amounts of free acid, or when the double cyanides are used, equal quantities of free potassium cyanide. And, moreover, that the two cathodes and also the two anodes should be of the same size, and that the distance between the anode and cathode should be the same in both solutions. These conditions were closely observed throughout this work.

ARRANGEMENT OF APPARATUS.

The deposits in this series of experiments were made in two platinum dishes of equal capacity and equal internal area. The anode in each case consisted of a coil of rather large platinum wire, the two coils being of the same shape and size. The dishes were insulated from each other by means of two glass stands.

The platinum coils were completely immersed in the solutions and the portion of the wire near the surface of the liquid was covered with paraffin to prevent surface contact. The current, after passing through the two solutions, was allowed to pass through a hydrogen voltameter in order that its strength might be observed at any time.

In the second arrangement of apparatus the platinum dishes were made the anodes, and two pieces of platinum foil of the same shape and size were used for the cathodes. The results, however, from this second arrangement were not as satisfactory as from the first.

MODE OF PROCEDURE.

A solution of the double cyanide of silver and potassium was placed in one of the platinum dishes and a solution of the double cyanide of mercury and potassium in the other. The quantities of silver and mercury present in their solutions were approximately proportional to their equivalent weights. Each solution contained a slight excess of potassium cyanide. The dishes were placed in their positions and the anodes immersed sometime before the current was allowed to act. When the temperature of the two solutions was the same as that of the room, the connection was made and the same current allowed to pass through the two solutions. The quantity of metal deposited was never allowed to exceed one-half of the metal present in the solution at first. Before interrupting the current, the solutions were siphoned from the two platinum dishes at the same time with two siphons of the same bore. The deposits were then washed several times with boiling water, carefully dried and their weights determined. Experiments were made with currents of different strength and with solutions of various degrees of concentration. The results obtained were far from being satisfactory. The strength of current which seemed best adapted to the work was that which deposited about one-tenth of a gram of silver per hour.

From a large number of experiments, only seven results were obtained which seem of any value in determining the atomic mass of mercury. And it must be added that many others were rejected, not because they were known to be vitiated in any way, but because the results obtained for the atomic mass of mercury differed from those obtained by other methods. It is possible that, in a large number of experiments, the condition would be more favorable in some than in others, but whether the close agreement of the results selected was due to this or to the balancing of errors, could not be determined.

Seven results computed on the basis of 107.92 for the atomic mass of silver are as follows:

	Weight of Hg. Gram.	Weight of Ag. Gram.	Atomic mass of mercury.
1	0.06126	0.06610	200.036
2	0.06190	0.06680	200.007
3	0.07814	0.08432	200.021
4	0.10361	0.11181	200.011
5	0.15201	0.16402	200.061
6	0.26806	0.28940	199.924
7	0.82808	0.89388	199.929

Mean = 199.996
Maximum = 200.061
Minimum = 199.924

Difference = 0.137

Computing from the total quantities of mercury and silver obtained, we have 199.971 for the atomic mass of mercury.

Although the cause of the large variation in the rejected observations could not be definitely determined, several sources of error suggest themselves.

First, small quantities of hydrogen were undoubtedly set free in the process of electrolysis, and unless these quantities were always equal in the two solutions, which is not probable, an error would be introduced.

Second, in some solutions an error might easily be introduced by a change in the atomicity of mercury, but in a solution of the double cyanide of mercury and potassium this change is hardly probable.

Third, the occlusion of hydrogen by the two metallic deposits would also be a possible source of error; but only small errors could be introduced in this way.

To account for the difference of several units in the results, the source of error first mentioned seems by far the most probable.

SUMMARY.

In the discussion of the results obtained in the different series of observations on the compounds of silver, the probable sources of error and likewise the advantages of the method were pointed out. The same discussion applies equally well to the observations on mercury.

It is evident that the first three series of observations on mercury are entitled to more weight than the last series. Just why the results on mercuric bromide should be lower than those on mercuric chloride is not clear. Both compounds are certainly well adapted to atomic mass determinations, inasmuch as they can be purified by both crystallization and sublimation. The most probable impurity in mercuric bromine would be mercuric chloride, but that would tend to increase rather than lower the results. The series of observations on mercuric cyanide have, perhaps, one advantage over the others, in that no potassium cyanide was used. The results obtained in this series are still higher than those obtained from mercuric chloride and almost two-tenths of a unit higher than those obtained from mercuric bromide. However, as the same care was exercised in the purification of the material for each of the three series, and as there was no apparent error in either case, equal weight must be given to each of the three series in determining the most probable value of the atomic mass of mercury. And, as the mean of the last series is almost identical with the mean of the first three, equal weight can be given to this series without introducing any error.

Computing the general mean from the separate observations, we have:

	Atomic mass of mercury.
First series	200.006
Second "	199.883
Third "	200.071
Fourth "	199.996

General mean = 199.989

From the total quantities of material used and metal obtained, the general mean is :

	Atomic mass of mercury.
First series	199.996
Second "	199.885
Third "	200.070
Fourth "	199.971
General mean =	199.981

Combining this with the first general mean we have :

Atomic mass of mercury.

First general mean = 199.989

Second " " = 199.981

Most probable mean of all the results = 199.985

or 200 for the atomic mass of mercury.

PART III.

DETERMINATION OF THE ATOMIC MASS OF CADMIUM.

Nine experimenters have determined the atomic mass of cadmium by many different methods, but the large variations in the results given by different chemists leave the true value of this constant still uncertain.

Stromeyer[1] gave no details of his method of operation, but found that 100 parts of cadmium combined with 14,352 parts of oxygen. On the basis of O = 16, this ratio gives 111.483 for the atomic mass of cadmium. This result is much lower than those obtained by other experimenters and is perhaps only of historical interest.

In a series of nine experiments, Von Hauer[2] determined the ratio of cadmium sulphate to cadmium sulphide. The sulphate used was purified by repeated recrystallizations and was finally dried at a temperature of 200°. After weighing the sulphate was always dried a second time and reweighed. The two weighings never differed as much as one milligram. The sulphide obtained was in each case tested for sulphate. The reduction of the sulphate to sulphide was accomplished by heating

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[1] Berzelius' Lehrbuch, 5th Ed., 3, 1219.

[2] *J. prakt. Chem.*, 72, 350.

the sulphate in a current of dry hydrogen sulphide under pressure. The mean of nine observations computed on the basis O = 16 and S = 32.06 gives 111.93 for the atomic mass of cadmium. Considering the large quantity of material used each time and the precautions taken to insure accuracy, there seems to be little objection to the method.

Dumas[1] determined the ratio of cadmium chloride to metallic silver by titrating a solution containing a weighed quantity of cadmium chloride with a silver nitrate solution of known strength. The cadmium chloride was prepared by dissolving metallic cadmium in boiling hydrochloric acid. The solution was evaporated to dryness and the chloride fused for six hours in a current of hydrochloric acid gas. The mean of six determinations gives 112.24 for the atomic mass of cadmium (O = 16).

Maximum result, Cd = 112.759
Minimum " Cd = 111.756
Difference = 1.003

This large variation in the results obtained indicates the presence of impurities in the material used. In the first three experiments the cadmium was not purified; the mean of these three is Cd = 112.476. The metal used in the last three experiments was considered by Dumas to be absolutely pure; the mean of the last three results is Cd = 112.007. From the degree of purity of the cadmium chloride used in the different experiments, Dumas was inclined to reject the higher results and concluded that the true atomic mass of cadmium was about 112.

Lensen[2] prepared pure cadmium oxalate by precipitating a solution of cadmium chloride, purified by repeated crystallization, with pure oxalic acid. The precipitate was washed and carefully dried at a temperature of 150°. The mean of three results obtained by converting a weighed portion of the oxalate to oxide gives 112.06 for the atomic mass of cadmium (O = 16). The small quantity of material used in the different experiments is somewhat objectionable.

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[1] *Ann. chim. phys.*, [3], 55, 158.
[2] *J. prakt. Chem.*, 79, 281.

Huntington,[1] under the direction of Cooke, determined the ratio of cadmium bromide to silver bromide and also the ratio of cadmium bromide to metallic silver. The bromide used was prepared by dissolving cadmium carbonate, which had been carefully purified, in pure hydrobromic acid. The product obtained was dried at a temperature of 200° and finally sublimed in a porcelain tube in a current of dry carbon dioxide. In the first series of experiments the silver bromide corresponding to the cadmium bromide used was weighed. The mean of eight determinations computed from the total quantity of material used and silver bromide obtained, on the basis of Ag = 107.93 and Br = 79.95 is Cd = 112.24. In the second series of experiments the quantity of metallic silver required to precipitate a known quantity of cadmium bromide was determined. The mean of eight determinations computed as in the first series gives 112.245 for the atomic mass of cadmium. The separate determinations in both series agree very closely.

Partridge[2] made three series of determinations. The first depended upon the conversion of cadmium oxalate into oxide, the second, on the reduction of the sulphate to sulphide, and the third, on the conversion of the oxalate into sulphide. The cadmium used in these experiments was purified by distilling twice *in vacuo*. Ten observations on the conversion of the oxalate into oxide, computed on the basis of O = 16 and C = 12, give 111.801 as a mean for the atomic mass of cadmium. Recalculated by Clarke,[3] on the basis of O = 16 and C = 12.005, the atomic mass of cadmium becomes 111.818. The mean of ten results obtained by reducing the sulphate to sulphide, computed on the basis of O = 16 and S = 32, gives 111.797 for the atomic mass of cadmium. Recalculated by Clarke on the basis of O = 16 and S = 32.074, the atomic mass of cadmium is 111.711. In the third series the oxalate of cadmium was converted into sulphide by heating in a current of dry hydrogen sulphide. The mean of ten determinations, computed on the basis of O = 16 and S = 32, gives 111.805 for the atomic mass of cadmium.

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[1] *Proc. Amer. Acad.*, 17, 28.

[2] *Am. J. Sci.*, [3], 40, 377.

[3] *Am. Chem. J.*, 13, 34.

Recalculated by Clarke on the basis of O = 16 and S = 32.074, the mean becomes 111.589. Partridge gives 111.8 for the atomic mass of cadmium, as a mean of the three series. If the higher values for carbon and sulphur be introduced this value becomes somewhat lower.

Jones[1] determined the atomic mass of cadmium by two different methods. The first was based on the conversion of the metal into oxide, and the second on the conversion of the oxalate into oxide. The cadmium used was distilled six times *in vacuo*. The last distillate was tested spectroscopically and found to be free from impurities. In the first series of experiments a weighed portion of the pure metal was dissolved in pure nitric acid in a porcelain crucible. The solution was evaporated to dryness and the resulting cadmium nitrate ignited to oxide. The final decomposition was accomplished by means of a blast lamp. Reducing gases were carefully excluded from the crucible during the process of ignition. The weighings were all made against a tared crucible. The mean of ten observations, computed on a basis of O = 16 gives 112.07 for the atomic mass of cadmium. The different determinations agree very closely. In the second series of experiments cadmium oxalate, prepared by precipitating pure cadmium nitrate with pure oxalic acid, was converted into oxide. The material was carefully ignited until the oxalate was decomposed; it was then treated with nitric acid and again ignited in a manner similar to that described in the first series. The mean of five determinations computed on the basis of O = 16 and C = 12.003 is Cd = 111.032. From all the observations, Jones concludes that 112.07 represents very closely the atomic mass of cadmium (O = 16).

Lorimer and Smith[2] determined the ratio of the atomic mass of cadmium to that of oxygen by dissolving pure cadmium oxide in potassium cyanide and electrolyzing the solution. To obtain pure material, the commercial cadmium was dissolved in nitric acid and the solution evaporated to crystallization. The crystals of cadmium nitrate were removed from the liquid, dissolved in pure water and recrystallized. The product obtained by the

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[1] *Am. Chem. J.*, 14, 261.

[2] *Ztschr. anorg. Chem.*, 1, 364.

second recrystallization was dissolved in a little water and treated with a slight excess of potassium cyanide in a platinum dish. From this solution the metallic cadmium was thrown out by means of the electric current. The nitrate obtained by dissolving the electrolytic cadmium in pure nitric acid was tested spectroscopically and found to be free from impurities. The pure cadmium nitrate was digested with ammonium hydroxide and ammonium carbonate and the resulting cadmium carbonate ignited to oxide in a platinum crucible. The method of operation was very simple, a weighed portion of the oxide was dissolved in pure potassium cyanide, the solution electrolyzed and the resulting metallic cadmium weighed. The mean of nine observations computed on the basis of O = 16 gives 112.055 for the atomic mass of cadmium.

Bucher[1] made six series of experiments. The cadmium used was purified by nine distillations *in vacuo*. The weighings were all reduced to a vacuum standard and computed on the basis of O = 16, S = 32.059, C = 12.003, Cl = 35.45, Br = 79.95, and Ag = 107.93.

In the first series cadmium oxalate, dried for fifty hours at 150°, was ignited to oxide. The mean of eight observations gives 111.89 for the atomic mass of cadmium.

In the second series, cadmium oxalate was converted into sulphide by heating in a current of dry hydrogen sulphide. The mean of four determinations is Cd = 112.15.

In the third series a weighed quantity of cadmium chloride, dried at a temperature of 300° in hydrochloric acid gas, was precipitated with silver nitrate and the resulting silver chloride weighed. The mean of twenty-one determinations is Cd = 112.39. The separate observations in this series agree very closely.

The fourth series was similar to the third, except that cadmium bromide was used instead of the chloride. The mean of five determinations is Cd = 112.38, a result almost identical with that obtained from the chloride.

In the fifth series a weighed portion of metallic cadmium was converted into sulphate, which was dried at 400° and weighed.

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[1] Thesis, Johns Hopkins University, *1894*.

The excess of sulphuric acid which remained with the sulphate was estimated and its weight deducted. The only result given is Cd = 112.35.

In the last series metallic cadmium was converted into oxide by dissolving in nitric acid and igniting the resulting cadmium nitrate. The mean of two determinations made by igniting the material in a porcelain crucible gives 112.08 for the atomic mass of cadmium. Three similar determinations made with a platinum crucible gave, as a mean Cd = 111.87. From a series of experiments on cadmium oxide, Bucher concluded that a correction should be applied to the last and also the first series. By making this correction, the results in these two series would be very close to those obtained from the chloride and bromide.

From all the preceding determinations Clarke gives 111.93 as the most probable value for the atomic mass of cadmium. The large variation in the results of different experimenters has not been fully explained. Some chemists think that the larger values are due to a higher degree of purity in the metallic cadmium used, and hence regard these values as being more nearly correct. But it must be remembered that the reverse is true in the experiments of Dumas. From material which had not been purified, Dumas obtained results ranging from 112.32 to 112.76 for the atomic mass of cadmium, while from material which he considered absolutely pure, the results were from 111.76 to 112.13.

PREPARATION OF PURE CADMIUM.

The metallic cadmium used in these experiments was purified by distillation in a current of hydrogen which had been passed through solutions of caustic potash, lead nitrate, potassium permanganate, and sulphuric acid. A hard glass combustion tube was heated to redness and the walls of the tube indented at two points with a three-cornered file. This divided the tube into three parts. Commercial cadmium was placed in one end of the tube and connection made with the hydrogen generator. After complete removal of the air, the tube was carefully heated in a combustion furnace until one-half of the metal had distilled over into the middle portion of the tube. The metal was cooled in a current of hydrogen. The tube was then broken and the metal removed. The portions in the first and last sections of the tube were rejected. The middle portion was placed in a second combustion tube, similar to the first, and the distillation repeated. After three distillations the metal was examined spectroscopically and found to be free from impurities.

FIRST SERIES.

EXPERIMENTS ON CADMIUM CHLORIDE.

Dumas and Bucher have both determined the ratio of cadmium to chlorine in cadmium chloride. The results given for the atomic mass of cadmium by the latter experimenter are almost four-tenths of a unit higher than those given by the former.

PREPARATION OF CADMIUM CHLORIDE.

Hydrochloric acid was purified by first passing chlorine through the commercial C. P. acid to remove any sulphur dioxide; the excess of chlorine was removed by a current of carbon dioxide. The acid was then distilled from calcium chloride and the hydrochloric acid gas collected in pure water. Pure metallic cadmium was then dissolved in the acid and the solution evaporated to crystallization. The crystals of cadmium chloride were removed from the liquid and thoroughly dried. The material was then placed in a hard glass combustion tube, similar to that used in the distillation of metallic cadmium, and carefully sublimed in a current of dry carbon dioxide. The first and last portions of the sublimate were rejected. The middle portion, which consisted of pearly leaflets, was placed in a weighing tube and kept in a desiccator. As only a small quantity of the material could be sublimed at a time, the different analyses were made from different sublimations.

MODE OF PROCEDURE.

A weighed portion of the cadmium chloride was dissolved in a little water in a platinum dish. A slight excess of potassium cyanide was added and, after diluting to 200 cc. with pure water, the solution was electrolyzed. Before interrupting the current, the liquid was siphoned from a dish in a manner already outlined in the experiments on silver. The metallic deposit was washed several times with boiling water and carefully dried. The strength of the current and time of action were as follows:

Time of action.	Strength of current.
12 hours	$N.D_{100} = 0.1$ amperes.
4 "	$N.D_{100} = 0.15$ "
4 "	$N.D_{100} = 0.30$ "

The cadmium was thrown down as a dense white deposit.

Ten results on cadmium chloride reduced to a vacuum standard on the basis of:

3.3 = density of cadmium chloride,
8.55 = " " metallic cadmium,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $CdCl_2$, assuming 35.45 to be the atomic mass of chlorine, are as follows:

	Weight of $CdCl_2$. Grams.	Weight of Cd. Gram.	Atomic mass of cadmium.
1	0.43140	0.26422	112.054
2	0.49165	0.30112	112.052
3	0.71752	0.43942	112.028
4	0.72188	0.44208	112.021
5	0.77264	0.47319	112.036
6	0.81224	0.49742	112.023
7	0.90022	0.55135	112.041
8	1.02072	0.62505	112.002
9	1.26322	0.77365	112.041
10	1.52344	0.93314	112.078

Mean = 112.038
Maximum = 112.078
Minimum = 112.002

Difference = 0.076
Probable error = ±0.005

From the total quantity of material used and metal obtained, we have 112.040 for the atomic mass of cadmium.

SECOND SERIES.

PREPARATION OF CADMIUM BROMIDE.

The bromine used in this series was purified as outlined in the experiments on mercuric bromide. The cadmium bromide was prepared by allowing bromine water to act on metallic cadmium for several days at the ordinary temperature. When the action was complete, the solution was filtered and evaporated to crystallization. The crystals of cadmium bromide were removed from the liquid and thoroughly dried. The material was then placed in a hard glass combustion tube and carefully sublimed in a current of dry carbon dioxide. The first and last portions of the sublimate were rejected. The middle portion was removed from the tube, placed in a weighing bottle and kept in a desiccator. The product obtained in this way consisted of a crystalline, pearly leaflet which dissolved immediately in water without leaving a residue.

MODE OF PROCEDURE.

The method of operation was the same as for cadmium chloride. A weighed portion of the material was dissolved in a little water in a platinum dish. A slight excess of potassium cyanide was then added and after diluting to 200 cc. the solution was electrolyzed and the resulting metal weighed. The strength of current and time of action were the same as for cadmium chloride.

Ten observations on cadmium bromide reduced to a vacuum standard on a basis of:

4.8 = density of cadmium bromide,
8.55 = " " metallic cadmium,
21.4 = " " platinum dish,
8.5 = " " weights,

and computed for the formula $CdBr_2$, assuming 79.95 to be the atomic mass of bromine, are as follows:

	Weight of $CdBr_2$. Grams.	Weight of Cd. Gram.	Atomic mass of cadmium.
1	0.57745	0.23790	112.031
2	0.76412	0.31484	112.052
3	0.91835	0.37842	112.067
4	1.01460	0.41808	112.068
5	1.15074	0.47414	112.053
6	1.24751	0.51392	112.019
7	1.25951	0.51905	112.087
8	1.51805	0.62556	112.076
9	1.63543	0.67378	112.034
10	2.15342	0.88722	112.041

Mean = 112.053
Maximum = 112.087
Minimum = 112.019

Difference = 0.068
Probable error = ±0.005

From the total quantity of material used and the metal obtained, Cd = 112.053.

THIRD SERIES.

In these experiments an attempt was made to determine the ratio of the atomic mass of cadmium to that of silver by allowing the same electric current to pass successively through solutions of the two metals and weighing the resulting deposits. The arrangement of apparatus and the details of the method were described under the mercury silver series. The results were not as satisfactory as the corresponding results obtained for mercury. A large number of determinations were made with currents of different strength and solutions of different concentration, but the results were, in most cases, far below those obtained in the first two series. A current which deposited about twelve hundredths of a gram of silver per hour seemed to give the best results. From all the observations, five results were selected which differed only about one-tenth of a unit from those of the first two series. Results selected in this way are entitled to but little weight, and perhaps should not be used in determining the general mean of all the observations.

Computed on the basis of 107.92 for the atomic mass of silver, the only admissible results are as follows:

	Weight of Ag. Gram.	Weight of Cd. Gram.	Atomic mass of cadmium.
1	0.24335	0.12624	111.928
2	0.21262	0.11032	111.991
3	0.24515	0.12720	111.952
4	0.24331	0.12616	111.916
5	0.42520	0.22058	111.971

Mean = 111.952
Maximum = 111.991
Minimum = 111.916

Difference = 0.075

This method was discussed under mercury. The probable sources of error pointed out there apply equally well in the case of cadmium. Until the large variations can be accounted for and the difficulties overcome, the method must be regarded as unsatisfactory.

SUMMARY.

Inasmuch as but one method of analysis has been used throughout this work, it is useless to discuss it here. The advantages and objections pointed out under silver apply also to cadmium.

In summing up the work on cadmium, equal weight must be given to the first two series. The last series must be considered alone and all that need be said of it is, that the results obtained for the atomic mass of cadmium never exceeded 112. In the corresponding series on mercury, the variations were in both directions from 200.

The general mean of the first two series calculated from the separate observations is:

	Atomic mass of Cd.
First series	= 112.038
Second series	= 112.053
General mean	= 112.0455

From the total quantity of material used and metal obtained we have:

	Atomic mass of Cd.
First series	= 112.040
Second series	= 112.053
General mean	= 112.0465

Combining this with the first general mean we have 112.046 as the most probable result of all the work, for the atomic mass of cadmium. This result is lower than those obtained by Huntington and Bucher, but agrees very closely with the results obtained by von Hauer, Dumas, Lensen, Jones, and Lorimer and Smith.

I wish here to express my sense of gratitude to Professor Edgar F. Smith, at whose suggestion this work was undertaken and under whose personal supervision it was carried out.

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METAL SEPARATIONS BY MEANS OF HYDROCHLORIC ACID GAS.[1]

BY J. BIRD MOYER.

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INTRODUCTION.

THE action of gaseous haloid acids upon metallic oxides and their salts, is a field of investigation, which, though not of recent origin, has been but lately developed. It was Debray[2] who first called attention to the volatility of molybdic acid in a stream of hydrochloric acid gas, with the formation of $MoO(OH)_2Cl_2$.

E. Péchard[3] applied this and showed that molybdic acid was completely eliminated and separated from tungstic acid, by its volatility in a current of hydrochloric acid. Since that time nothing further has been done with single haloid acids, in gas form, until quite recently. Compounds have been decomposed, salts volatilized, and separations made, by means of other gases and mixtures, which may be as effective as hydrochloric acid, but are not devoid of trouble nor nearly so neat.

Smith and Oberholtzer[4] repeated and confirmed Péchard's

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[1] From author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Doctor of Philosophy. 1896.

[2] *Compt. rend.*, 46 1098, and *Ann. Chem.* (Liebig), 108, 250.

[3] *Compt. rend.*, 114, 173.

[4] *J. Am. Chem. Soc.*, 15, 1.

work in regard to the separation of molybdic acid from tungstic acid, and in addition showed that gaseous hydrobromic, hydriodic, and hydrofluoric acids acted similarly. Later, Smith and Maas[1] made use of the volatilization of molybdic acid for a close atomic mass determination of molybdenum.

Smith and Hibbs[2] showed that vanadium behaved like molybdenum. Hydrochloric acid gas completely eliminates vanadic acid from sodium vanadate. A little later they investigated the action of hydrochloric acid upon the members of Group V of the periodic system.[3]

The sodium salts of nitric, pyrophosphoric, pyroarsenic and pyroantimonic acids were used. They found nitrogen, arsenic, and antimony to be volatile in gaseous hydrochloric acid, and made it the basis of a separation of phosphoric acid from nitric acid. Lead arsenate changed completely to chloride, the arsenic being volatilized, thus affording a good quick separation. Smith and Meyer[4] tried the action of all the haloid acids upon the elements of Group V of the periodic system. They worked with sodium salts and observed: I. That nitrogen was expelled completely by all the haloid acids. II. That phosphoric acid was not acted upon. III. That arsenic acid was fully expelled by hydrochloric, hydrobromic, and hydriodic acids, but only partially by hydrofluoric acid. IV. That antimony was completely volatilized by hydrochloric acid. There was no work done on bismuth. V. Vanadium went over completely in hydrochloric acid, but only partially in hydrobromic and hydrofluoric acids. VI. Columbium forms volatile products with hydrochloric and hydrobromic acids. No knowledge of didymium was obtained. VII. Tantalum is only slightly volatile in hydrochloric acid.

P. Jannasch and F. Schmidt[5] repeated some of the work of Smith and Hibbs, in which they confirmed the separation of arsenic from lead. They anticipated a slight portion of my work, and in addition separated arsenic acid from iron, tin from

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[1] *Ztschr. anorg. Chem.*, 5, 280.

[2] *J. Am. Chem. Soc.*, 16, 578.

[3] *Ibid.*, 17, 682.

[4] *Ibid.*, 17, 735.

[5] *Ztschr. anorg. Chem.*, 9, 274.

lead, tin from copper, and tin from iron, in a stream of hydrochloric acid gas.

The position of bismuth in the periodic system makes it natural to suppose that it too will be volatile in hydrochloric acid gas. This I have shown to be true, and was thus enabled to separate it from lead and copper. The action of hydrobromic acid on bismuth trioxide was also tried; it formed the bromide and then volatilized. It requires a higher temperature and longer action than with hydrochloric acid. Because of lack of time, I have been compelled to abandon the experiments instituted with a view of affecting separations, in atmospheres of hydrobromic acid and hydriodic acid gas and have confined my labors to hydrochloric acid gas.

METHOD OF WORK.

The hydrochloric acid gas was generated by dropping concentrated sulphuric acid from a separatory funnel, upon concentrated hydrochloric acid contained in a three liter flask. The gas evolved at the ordinary temperature was dried by passing it through two sulphuric acid drying bottles and then through a calcium chloride tower, when it was considered sufficiently dry for the purpose. The substance to be acted upon was weighed out in a porcelain boat and the latter was placed in a combustion tube of hard glass.

The tube had previously been rinsed with alcohol and then with ether, to remove all moisture. The ether was removed by drawing a current of dry air through the tube. This tube was connected to a two-necked bulb receiver containing about 300 cc. of distilled water. When working with arsenic ten cc. of nitric acid were added. The connecting tube from the combustion tube to the bulb receiver was made to enter the receiver and dip below the surface of the water, thus catching all volatile products, as well as taking up the hydrochloric acid gas. To insure safety from the loss of volatile products, a small flask containing water was attached to the bulb receiver. The apparatus was controlled at both ends by stop-cocks. This is necessary to prevent backward suction on disconnecting the apparatus. After the reaction was completed the boat was removed to a sulphuric acid desiccator from which the air could be exhausted. In general, the procedure was similar to that employed by Hibbs.[1]

I.—BEHAVIOR OF ANTIMONY TRIOXIDE.

Antimony oxide, labelled chemically pure, was dissolved in hydrochloric acid and precipitated with a large amount of water. After washing by decantation it was redissolved and reprecipitated. This procedure was repeated several times, when it was precipitated by ammonium carbonate, washed, and ignited. The pure oxide obtained in this manner was subjected to the action of hydrochloric acid gas and it was found to volatilize completely. In each trial a one-tenth gram of the oxide was acted upon. The temperature varied between 150° and 190° C. It was determined in the following way: The combustion tube was slipped through two holes made in the sides of a copper drying oven.

A very slow current of gas was used as the antimony seemed to volatilize more readily and completely, if the current was slow and the heat gentle. This I attribute, on reflection, to the fact that I ignited the oxide too strongly, (to a red heat) in its preparation. It dissolved with difficulty in concentrated hydrochloric acid. Lack of time prevented the repetition of this experiment and the separation of antimony from lead and copper, in which this substance was used. About eight hours was the time required for the volatilization; very probably a shorter time would be required if the oxide had been obtained by gentle ignition.

II.—BEHAVIOR OF LEAD OXIDE.

Pure lead oxide was obtained from recrystallized nitrate, by careful ignition. This oxide changed completely into chloride at the ordinary temperature and it was only necessary to apply a gentle heat to complete the change and entirely remove the water formed. No volatilization was noticed until a temperature of 225° was reached; at this point the lead chloride slightly volatilized.

I think it possible to estimate lead as chloride, if the temperature is kept under 200°. A weighed amount of lead oxide was

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[1] Thesis, 1896.

acted upon by hydrochloric acid gas in the cold, for two hours, and then heated sufficiently to remove all the water formed.

The boat was cooled in the gas, and then placed in a sulphuric acid desiccator and allowed to stand one-half hour. It was then weighed.

EXPERIMENTS.

	Lead oxide taken. Gram.	Lead chloride obtained. Gram.	Lead chloride required. Gram.	Difference. Gram.
Experiment I	0.1017	0.1267	0.1267	0.0000
" II	0.1015	0.1258	0.1265	—0.0007
" III.....	0.1169	0.1454	0.1447	+0.0007

The lead chloride dissolved in hot water without residue.

III.—THE SEPARATION OF ANTIMONY FROM LEAD.

The oxides were carefully weighed and thoroughly mixed in a porcelain boat. Hydrochloric acid gas was passed over them in the cold, until the lead oxide had been entirely changed to the chloride. It was then heated with the smallest flame obtainable from a fish-tail burner, placed about two inches below the tube.

	Antimony trichloride taken. Gram.	Lead chloride taken. Gram.	Lead chloride obtained. Gram.	Lead chloride required. Gram.
Experiment I	0.1015	0.1189	0.1470	0.1482
" II....	0.1090	0.1021	0.1266	0.1272
" III...	0.1350	0.0852	0.1057	0.1062
" IV ...	0.1250	0.1671	0.2069	0.2083

The time required was seven hours. The lead chloride was immediately weighed. It dissolved completely in hot water and this solution was tested by means of Marsh's apparatus for antimony, without finding the latter present. Experiment II was slightly varied by first moistening the oxides with a drop of hydrochloric acid.

IV.—BEHAVIOR OF BISMUTH OXIDE.

Bismuth nitrate, as pure as could be obtained, was dissolved in nitric acid and then thrown down with a large quantity of water. The precipitate was carefully washed by decantation. This operation was repeated several times.

It was then dissolved in acidulated water and precipitated with ammonium hydroxide and ammonium carbonate. This, on ignition, gave pure oxide, which, heated in a stream of hydrochloric acid gas, completely volatilized as chloride. Here the same treatment is necessary as obtained for antimony. A slow current of gas and a low heat were best adapted for the volatilization (a temperature of 130°, or roughly, the heat afforded by a fish-tail burner placed two inches below the combustion tube, with a flame an eighth of an inch high). The bismuth chloride sublimed nicely, forming a white crystalline mass beyond the boat, which could be readily driven along by a gentle heat.

V.—THE SEPARATION OF BISMUTH FROM LEAD.

The same material was used as in the preceding experiments. The weighed oxides were thoroughly mixed in a porcelain boat. Usually the gas was allowed to act in the cold for an hour, which changed the oxides completely to chlorides.

The same conditions prevailed as under bismuth oxide alone. If an attempt was made to hasten the reaction by heating higher than 180°, a little lead would volatilize. This sublimate, slightly yellow in color, would appear directly over the boat and could not be driven along the tube like bismuth, hence it was readily detected.

The separation of bismuth from lead requires much care, as it is not as sharp as could be desired. It is also difficult to tell exactly when the last traces of bismuth have been driven out of the boat, as there was no color change to indicate it, both metals forming white chlorides. The separation is complete in from six to seven hours. At the end of the separation the position of the boat was changed and the action continued; if no further sublimation occurred it was cooled and removed to a desiccator. The weight was taken after standing one-half hour over sulphuric acid. With care bismuth can be separated from lead in this manner.

	Lead oxide taken. Gram.	Bismuth trioxide taken. Gram.	Lead chloride obtained. Gram.	Lead chloride required. Gram.	Difference. Gram.
Experiment I	0.1014	0.2020	0.1261	0.1264	—0.0003
" II....	0.1006	0.0642	0.1252	0.1254	—0.0002
" III...	0.1038	0.1003	0.1294	0.1302	—0.0008
" IV ...	0.1412	0.1260	0.1759	0.1759	+0.0000

The chloride of lead dissolved completely in hot water. It showed no bismuth. The sublimate contained no lead.

VI.—BEHAVIOR OF CUPRIC OXIDE.

Pure copper nitrate was made by recrystallization. It was then ignited in a porcelain crucible at a dull red heat, until it became constant in weight. The pure black oxide was then subjected to the action of hydrochloric acid gas. In Experiment I, the boat containing the oxide was heated at the outset to 175°. It was taken out after two hours, placed over sulphuric acid for half an hour, and weighed. The weight showed that the copper oxide had hardly been acted upon. It had only been superficially changed to chloride. It was then moistened with two or three drops of hydrochloric acid, dried in a rapid current of the gas, and heated two hours longer. This resulted in the complete transformation into chloride. The anhydrous chloride thus obtained, liver brown in color, was placed in a desiccator from which the air was exhausted. This was done to remove all the gas that might be retained and prevented a too rapid absorption of moisture.

Copper chloride absorbs moisture but not so rapidly as to prevent weighing in this form.:

	Copper oxide taken.	Copper chloride obtained.	Copper chloride required.	Difference.
	Gram.	Gram.	Gram.	Gram.
Experiment I	0 1011	0.1708	0.1713	—0.0005
" II....	0.1025	0.1726	0.1736	—0.0010
" III...	0.1034	0.1756	0.1752	+0.0004

In Experiment II, the change was completed in the cold by prolonged action through four hours. It was then heated about ten minutes at the end to drive out the moisture that had formed. In all the experiments cited, the copper chloride, after weighing, was found to dissolve completely in cold water.

VII.—THE SEPARATION OF ANTIMONY FROM COPPER.

The same material was used as in the preceding experiments. The weighed oxides were thoroughly mixed. The antimony was completely volatilized, leaving copper chloride which was weighed as such. The volatile antimony chloride was caught in the bulb receiver at the end of the tube. The bulb and tube were washed out with acidulated water into a beaker and the antimony thrown down with hydrogen sulphide. The antimony sulphide was filtered, thoroughly washed, and while moist dissolved in strong hydrochloric acid. The hydrogen sulphide evolved was conducted into bromine water and oxidized to sulphuric acid, which was estimated as usual and the antimony calculated.

The length of time required was eight hours. On several occasions the experiment was interrupted at the end of four hours, but invariably the separation was incomplete and on dissolving out the copper chloride formed, black copper oxide and white antimony oxide were plainly evident. In some cases the mixture of oxides was moistened with a couple of drops of hydrochloric acid and then evaporated down in a stream of acid gas, by heating the tube over a water-bath. This treatment seemed to facilitate matters but it is not altogether advisable, because the copper chloride has a tendency to creep over the sides of the boat. It is quicker in the end to separate them in the dry condition, allowing plenty of time for the reaction. The copper chloride obtained was perfectly soluble in cold water and contained no antimony. It could readily be changed to oxide and weighed if thought necessary.

	Antimony trioxide taken.	Copper oxide taken.	Copper chloride obtained.	Copper chloride required.	Difference.
	Gram.	Gram.	Gram.	Gram.	Gram.
Experiment I	0.1068	0.1040	0.1750	0.1745	+0.0005
" II	0.1062	0.1053	0.1774	0.1784	—0.0010
" III	0.1022	0.1020	0.1726	0.1728	—0.0002
" IV	0.1198	0.1020	0.1722	0.1728	—0.0006

	Antimony trioxide taken.	Antimony trioxide found.	Difference.
	Gram.	Gram.	Gram.
Experiment I	0.1068	0.1059	+0.0009

VIII.—THE SEPARATION OF BISMUTH FROM COPPER.

The pure oxides were mixed and treated as directed under bismuth and lead.

	Copper oxide taken. Gram.	Bismuth trichloride taken. Grams.	Copper chloride obtained. Grams.	Copper chloride required. Grams.	Difference. Grams.
Experiment I ..	0.1030	0.1069	0.1738	0.1745	—0.0007
" II..	0.1004	0.1077	0.1701	0.1713	—0.0012
" III.	0.1026	0.1060	0.1741	0.1738	+0.0003
" IV .	0.1019	0.1058	0.1718	0.1726	—0.0008

	Bismuth trioxide obtained. Gram.	Bismuth trioxide required. Gram.	Difference Gram.
Experiment I..............	0.1076	0.1069	+0.0007

The time required in each of these trials was seven hours. It seemed to be advantageous to raise the temperature and heat sharply for about ten minutes at the end, to insure the complete removal of the bismuth.

Moistening with acid helped the reaction but subjected it to the same danger of creeping as noted under antimony and copper.

The bismuth was estimated as follows: It was washed out of the tube and bulb with acidulated water and then precipitated as sulphide. The bismuth sulphide was filtered, washed, and dissolved in nitric acid. It was thrown out of the solution with ammonium hydroxide and ammonium carbonate, as hydrated oxide, and then filtered, dried, and ignited. It was weighed as oxide. The residue of copper chloride in the boat dissolved in cold water and showed no bismuth.

IX.—ACTION OF GASEOUS HYDROCHLORIC ACID ON SODIUM PYROARSENATE.

Hibbs[1] showed that arsenic was completely volatilized from sodium pyroarsenate, leaving weighable sodium chloride. In fact, so clean was the elimination of arsenic that he made it the basis of an arsenic atomic mass determination, with admirable success.

In working up the separation of arsenic from other metals it was necessary to start with the pure sodium salt. After purification I decided to test it, by weighing the salt produced by the action of the acid gas upon it. Several determinations gave close results, proving the salt pure.

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[1] See next paper, page 1044.

Chemically pure arsenate was procured. It was recrystallized and then ignited (not too strongly) for an hour. The pyroarsenate obtained was used in precipitating the various arsenates investigated.

	Sodium pyroarsenate taken. Gram.	Sodium chloride obtained. Gram.	Sodium chloride required. Gram.
Experiment I	0.2021	0.1330	0.1335
" II	0.1039	0.0691	0.0686

X.—THE SEPARATION OF ARSENIC FROM COPPER.

Pure sodium pyroarsenate was used to precipitate the copper salt.

Copper sulphate was recrystallized five times, a few good crystals were dissolved and the two solutions mixed. A green copper arsenate was precipitated. It was washed and dried at 100°. Salkowski[1] observes that copper arsenate still contains water above 130°. My salt had the composition $Cu_3As_2O_8 + 2H_2O$.

Hydrochloric acid gas completely changes it in the cold to chloride. A slight heat drives out the arsenic and water and leaves a brown anhydrous copper chloride, which can be weighed as such. Care was taken to remove all the acid gas before weighing.

The arsenic was washed out of the bulb into a beaker, this was warmed with nitric acid to insure oxidation, and then it was precipitated from an ammoniacal solution with "a magnesia mixture." It was weighed as $Mg_2As_2O_7$.

	Copper arsenate taken. Gram.	Copper chloride obtained. Gram.	Copper chloride required. Gram.	Difference. Gram.
Experiment I	0.1067	0.0850	0.0851	—0.0001
" II	0.1240	0.0998	0.0991	+0.0007
" III	0.1072	0.0860	0.0856	+0.0004
" IV	0.1155	0.0924	0.0923	+0.0001
" V	0.1042	0.0832	0.0833	—0.0001

Experiment I. As_2O_5 obtained, 0.0498 gram; As_2O_5 required, 0.0487 gram.

The residue of copper chloride completely dissolved in water. It showed no arsenic when tested in a Marsh apparatus.

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[1] *J. prakt. Chem.*, 104, 129.

XI.—THE SEPARATION OF ARSENIC FROM SILVER.

Silver arsenate was made by precipitating silver nitrate with sodium arsenate. Care was taken to have the nitrate in excess. The reddish-brown arsenate of silver was washed with boiling water, until the washings no longer showed silver, when tested with hydrochloric acid. It was dried at 110°.

As was expected, the acid gas attacked it even in the cold. In fact the action was so vigorous that a couple of analyses were spoiled by spattering. The trouble arose from the fact that the arsenate was not finely powdered. Heat was generated in the reaction sufficiently to send over a portion of the water formed. Experiment I was run in the cold for one hour and then heated sharply, for a few minutes, to expel the arsenic and water. The result was only 0.46 per cent. too high, but indicated that the salt should be heated longer, and not necessarily as high to remove all the arsenic.

The succeeding experiments were heated from one to two hours at 150° with better results:

	Silver arsenate taken. Gram.	Silver chloride obtained. Gram.	Silver chloride required. Gram.	Difference. Gram.
Experiment I	0.2542	0.2381	0.2363	+0.0018
" II	0.2325	0.2163	0.2161	+0.0002
" III	0.2084	0.1952	0.1938	+0.0014
" IV	0.2070	0.1927	0.1924	+0.0003

Experiment 1. Ag obtained = 70.45 per cent; Ag required = 69.99 per cent.

The residues in Experiments II, III, and IV were dissolved and tested for arsenic. None was found.

XII.—THE SEPARATION OF ARSENIC FROM CADMIUM.

Chemically pure cadmium sulphate was precipitated by a solution of sodium pyroarsenate. Stirring brought out a gelatinous arsenate, which changed by additional stirring to a granular salt. This was thoroughly washed and dried at 110°. It had the composition $Cd_3As_2O_8 + 2H_2O$. Salkowski[1] observes that a red heat is necessary to fully dehydrate this salt.

The moisture and arsenic were completely expelled at 150°,

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[1] *Loc. cit.*

leaving a uniform mass of cadmium chloride. It was weighed as such after standing over sulphuric acid for one-half hour. The arsenic was determined as usual.

	$Cd_3As_2O_8 + 2H_2O$ taken.	Cadmium chloride obtained.	Cadmium chloride required.	Difference.
	Gram.	Gram.	Gram.	Gram.
Experiment I....	0.2359	0.1965	0.1977	—0.0012
" II ...	0.1166	0.0968	0.0968	—0.0000
" III...	0.1030	0.0857	0.0855	+0.0002
" IV ...	0.1138	0.0947	0.0946	+0.0001
" V....	0.1043	0.0870	0.0867	+0.0003

	$Cd_3As_2O_8 + 2H_2O$ taken.	As_2O_5 obtained.	As_2O_5 required.	Difference.
	Gram.	Gram.	Gram.	Gram.
Experiment I....	0.2359	0.0813	0.0822	0.0009

The cadmium chloride dissolved perfectly in water and showed no arsenic, when tested in a Marsh apparatus.

XIII.—THE ACTION OF HYDROCHLORIC ACID GAS ON FERRIC OXIDE.

Pure oxide of iron was heated in a stream of acid gas. The behavior of iron is rather peculiar, as it very readily changes into chloride, and then only partially volatilizes. On heating to 200° the greater part is driven over as flaky crystals of ferric chloride. The remainder consists of a white mass, which refuses to go over on prolonged action and also on raising the temperature.

This residue was soluble in water and did not react with potassium thiocyanate, but immediately gave a blue precipitate with ferricyanide. Reduction was therefore evident; this is also noted by Jannasch and Schmidt.[1] The temperature at which ferric chloride usually goes into the ferrous condition is above 1000°.

Care was taken to prepare perfectly pure hydrochloric acid gas. Chemically pure acids were used to this end. The action however was the same in all cases.

XIV.—THE SEPARATION OF ARSENIC FROM IRON.

Chemically pure ferrous ammonium sulphate was carefully

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[1] *Loc. cit.*

oxidized with nitric acid, it was taken up in water, filtered and then crystallized several times. The best crystals were selected and a solution made to precipitate the arsenate. A white precipitate tinged with yellow was formed. It was washed by decantation and then filtered and washed until the washings no longer gave Prussian blue with ferrocyanide. It was then dried and gently ignited.

The acid gas acts on it quickly in the cold and it becomes a light green liquid. In evaporating off the moisture the chloride of iron was carried over with the arsenic.

In a second trial, with the temperature lower and occasionally removing the source of the heat altogether, when ebullition threatened to cause spattering, ferric chloride was obtained without loss. This was gradually heated a little higher to remove all the arsenic.

The chloride of iron was dissolved, oxidized, precipitated with ammonium hydroxide and estimated as usual. The result was fair and the product tested showed the absence of arsenic, but all succeeding experiments failed. Either the substance spattered or the iron went along with the arsenic.

Jannasch and Schmidt[1] separated arsenic from iron by placing their material in a large hard glass bulb and evaporating down to dryness with nitric acid, in an air current. This is not applicable when a porcelain boat is employed. They then volatilized the arsenic in hydrochloric acid gas at 120°.

XV.—SEPARATION OF ARSENIC FROM ZINC.

In some preliminary work zinc oxide was treated with acid gas at 200°. It completely changed to chloride and was not volatile. Pure zinc sulphate was used to precipitate the arsenate; it was washed, dried and ignited to 150°. The same difficulty appeared as was encountered under iron. Zinc arsenate melts down to a liquid mass as soon as the acid gas strikes it, which is extremely hard to evaporate without spattering. A small glass cover was placed over the boat, which tended to lessen the spattering, but did not entirely prevent it.

The zinc was estimated by taking the chloride up in a little

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[1] *Loc. cit.*

hydrochloric acid and running it down with pure mercuric oxide. It was then ignited and weighed as zinc oxide. One good result was obtained, but generally the residues of zinc contained arsenic and the results were far from being concordant.

XVI.—THE SEPARATION OF ARSENIC FROM COBALT AND NICKEL.

Cobalt and nickel were precipitated as arsenates in the usual manner, with a solution of pyroarsenate.

Cobalt nitrate, a Merck preparation, was carefully purified; considerable manganese was found and eliminated.

This gave the pink salt $Co_3As_2O_8 + 8H_2O$, which was ignited to the blue anhydrous compound.

Cobalt arsenate is very readily attacked by the acid gas in the cold, yielding a pink chloride. A slight heat, not much above 120°, changed it to the blue chloride and drove out the arsenic. At first it was quickly weighed as chloride, then it was taken up in a little hydrochloric acid and evaporated down with mercuric oxide. On ignition, black Co_3O_4 was obtained and weighed.

The arsenic was estimated as usual.

	Experiment I. Gram.	Experiment II. Gram.
$Co_3As_2O_8$ taken	0.1509	0.2029
$CoCl_2$ obtained	0.1309	....
$CoCl_2$ required	0.1293	....
Co_3O_4 obtained	0.0738	0.0969
Co_3O_4 required	0.0731	0.0983
Difference	+0.0007	—0.0014
As_2O_5 obtained	0.0770	....
As_2O_5 required	0.0764	....
Difference	+0.0006	....

On testing the cobalt residue by the Marsh test, no trace of arsenic was found. No cobalt was found in the sublimate. Some of the first experiments gave cobalt too low; it was thought that they had been heated too high, but testing showed *no* volatilized cobalt.

A temperature of 125° is sufficient to drive out all of the arsenic, and at this temperature there is no danger of volatilizing the cobalt.

In working with nickel, the green arsenate was simply dried in the first experiment. It therefore had the composition $Ni_3As_2O_8 + 8H_2O$.

Hydrochloric acid gas attacked it in the cold. A slight heat drives out the arsenic and moisture and leaves a salmon-colored chloride. The nickel chloride was changed to oxide by evaporating it with nitric acid and igniting.

	Experiment I. Gram.
$Ni_3As_2O_8 + 8H_2O$ taken	0.1502
NiO obtained	0.0554
NiO required	0.0561
Difference	—0.0007

In Experiments II and III the salt was made anhydrous by ignition.

	Experiment II. Gram.	Experiment III. Gram.
$Ni_3As_2O_8$ taken	0.1166	0.1040
NiO obtained	0.0577	0.0523
NiO required	0.0575	0.0513
Difference	+0.0002	+0.0010
As_2O_5 obtained	....	0.0515
As_2O_5 required	....	0.0526
Difference	....	—0.0011

The Marsh test showed no arsenic with the nickel.

XVII.—BEHAVIOR OF MINERALS IN HYDROCHLORIC ACID GAS.

Niccolite. One-half gram of the mineral was finely powdered and subjected to the action of acid gas for a day, at a temperature of 200° C. It was only very slightly affected.

A second portion was dissolved in nitric acid and evaporated down in a porcelain dish. It was then transferred to a boat and evaporated to dryness. To remove all the acid, it was heated in an oven to 110° for one-half hour. The dry substance was acted upon by the acid gas in the cold for five hours. It changed completely to chloride. A temperature of 150° for an hour removed all the moisture and arsenic.

The nickel chloride was evaporated down with nitric acid, ignited, and weighed as NiO. The arsenic was estimated as usual.

	Per cent.
Nickel found	43.79
Nickel calculated	43.60
Difference	0.19
Arsenic found	56.66
Arsenic calculated	56.40
Difference	0.26

Undoubtedly there is still a wide field open in regard to the behavior of hydrochloric acid gas upon mineral species. Smith and Hibbs[1] showed that mimetite lost its arsenic quantitatively, when heated in a stream of acid gas. In this laboratory others are being investigated with favorable indications. The direct employment of hydrochloric acid gas upon a powdered mineral would simplify many a tedious gravimetric process, leaving the separated elements in a desirable condition for further treatment.

In the case of a mineral such as niccolite, where it must first be decomposed with nitric acid and then transferred to a boat, the advantage is not so great. This, however, can be modified, so that the time factor is reduced and the advantage of the method still retained. Instead of using a boat, which has no advantage unless the non-volatile chlorides are to be weighed directly, a hard glass bulb can be substituted. The mineral is placed in the bulb, dissolved in nitric acid, and evaporated down by the aid of a current of air drawn through the bulb.

The residual oxides are then separated in a stream of hydrochloric acid gas as usual.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 15.]

THE ATOMIC WEIGHTS OF NITROGEN AND ARSENIC.[2]

BY JOSEPH GILLINGHAM HIBBS.

Received September 26, 1896.

THE atomic weight of the metal molybdenum had been determined by expelling molybdic acid from sodium molybdate with hydrochloric acid gas, then weighing the residual sodium chloride.

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[1] *Loc. cit.*

[2] From author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Doctor of Philosophy, 1896.

Having found that nitric acid and arsenic acid were driven from their alkali salts with ease, leaving a chloride that was absolutely pure, and believing that the atomic masses of nitrogen and arsenic determined in this manner would afford a valuable contribution to the literature relating to these constants, a carefully conducted series of experiments was made with two nitrates and one arsenate. The results are given in detail in the following lines:

THE ATOMIC WEIGHT OF NITROGEN.

In the past, determinations of the atomic weight of nitrogen have been made from the density of the gas itself, from the ratio between ammonium chloride and silver, and from the decomposition of certain nitrates. The first method in particular has been frequently applied. Thomson, Dulong, Berzelius, and Lavoisier brought to light many new facts relating to the atomic weight of nitrogen; unfortunately, however, considerable that they have presented has been affected by complications that have introduced inaccuracies.

Dumas and Boussingault[1] found the mean density of nitrogen to be 0.972; for hydrogen they found a mean density of 0.0693, which would give nitrogen an atomic weight of 14.026. Regnault obtained a more concordant series of results, the mean being 0.97137, and a density for hydrogen of 0.0692, which makes the atomic weight of nitrogen equal to 14.0244.

Clarke gives in detail his computation of the means of the results obtained by Penny, Stas, and Marignac. Their work on the determination of the atomic weight of this particular element was mainly on the ratio of ammonium chloride and silver, and the decomposition of certain nitrates. A great degree of accuracy was maintained throughout the entire investigation; but the amount of work required to obtain a single result necessarily lays the method open to a serious error of manipulation.

In this connection a paragraph from Clarke's "A Recalculation of the Atomic Weights" may be cited: "The general method of working upon these ratios is due to Penny. Applied to the ratio between the chloride and nitrate of potassium, it is

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[1] *Compt. rend.*, 1841—12. 1005.

as follows: A weighed quantity of the chloride is introduced into a flask which is placed upon its side and connected with a receiver. An excess of pure nitric acid is added, and the transformation is gradually brought about by the aid of heat, the nitrate being brought into a weighable form. The liquid in the receiver is also evaporated, and the trace of solid matter which has been mechanically carried over, is recovered and also taken into account."

The method indicated in this study, and actually applied with the results appended, is decidedly less objectionable. In this method there is no distillation, no precipitate, in fact, nothing that could involve serious error.

Clarke summarizes the results of Penny, Stas, and Marignac as follows:

1. From specific gravity of N.................. N = 14.0244
2. " ammonium chloride.................. N = 14.0336
3. " ratio number four.................... N = 14.0330
4. " silver nitrate........................ N = 13.9840
5. " potassium nitrate.................. . N = 13.9774
6. " sodium nitrate...................... N = 13.9906

Mean of results for N .... N = 14.0210

If oxygen is 16, this becomes 14.0291. Stas found the atomic weight of nitrogen to be 14.044. Dumas found 14 by experiments on the combustion of ammonia and cyanogen (O = 16). Pelouze found 14.014 by bringing a known weight of silver nitrate in contact with a known and slightly excessive weight of ammonium chloride, which excess was titrated. Anderson found 13.95 by the decomposition of the nitrate of lead, with just enough heat for decomposition (the same method that was used by Berzelius). Marignac found 14.02 by dissolving a known weight of silver in nitric acid and then melting and weighing the nitrate found.

A.—ATOMIC WEIGHT OF NITROGEN BY ACTION OF HYDROGEN CHLORIDE UPON POTASSIUM NITRATE.

The purest salt obtainable was dissolved in water, filtered, and recrystallized six times, a solution of which was tested for chlorides, sulphates, etc., but no impurity was found. One more crystallization was made and the best crystals were selected. These were washed with distilled water and dried at 210° C. for three hours, powdered, and again dried, and finally placed in a weighing bottle. This compound was dried before each experiment. It was also allowed to stand in a balance case one hour before weighing. The same degree of care was exercised in the preparation of the boat for weighing.

The weighing bottle was placed on the scale pan and allowed to stand several minutes in order to regain its normal temperature. After weighing it was quickly opened and a portion of the salt removed to the boat and again closed and allowed to stand in the balance case for several hours before reweighing. The boat was then introduced into the combustion tube and the gas passed over it. The characteristic action took place. The only difference in the method of procedure adopted here and that described in the first section of this paper, was a longer time being given to complete the action, using a lower temperature, in order to do away with all possibility of fusion of the salt. It was then carefully removed to a vacuum desiccator and allowed to stand over night before weighing. It may be said also that experiments were only conducted on clear days to insure the non-entrance of moisture.

With potassium nitrate, no great variation of amount was taken.

Five determinations were made in this case :

No.	Potassium nitrate taken. Gram.	Potassium chloride obtained. Gram.	Correction for potassium nitrate. Gram.	Correction for potassium chloride. Gram.	Correction for weight of potassium nitrate Gram.	Correction for weight of potassium chloride. Gram.	Molecular weight of potassium nitrate obtained.	Atomic weight of nitrogen obtained.
1.	0.11084	0.08173	0.00006	0.00004	0.11090	0.08177	0.101121	14.011
2.	0.14864	0.00960	0.00007	0.00005	0.14871	0.10965	0.101120	14.010
3.	0.21056	0.15525	0.00011	0.00008	0.21067	0.15533	0.101123	14.013
4.	0.23248	0.17214	0.00012	0.00009	0.23360	0.17223	0.101121	14.011
5.	0.24271	0.17894	0.00013	0.00009	0.24284	0.17903	0.101124	14.014

Atomic weight of nitrogen = 14.0118 ± 0.000472.

The atomic values used in these calculations were taken from "Table of Atomic Masses," revised by F. W. Clarke, in October, 1891.

The figures deduced from these values are, of course, subject to any change made by later revision of atomic weights. It is not so much the exact figure to which attention is called, as to the constancy of result brought forward by this method. The values used were :

Oxygen	16.00
Potassium	39.11
Chlorine	35.45
Specific gravity potassium nitrate	2.1
Specific gravity potassium chloride	1.99

B.—ATOMIC WEIGHT OF NITROGEN BY ACTION OF HYDROGEN CHLORIDE UPON SODIUM NITRATE.

The same degree of care and method of procedure were here observed as in Division A. The results are as follows :

No.	Potassium nitrate taken. Gram.	Sodium chloride obtained. Gram.	Correction for sodium nitrate. Gram.	Correction for sodium chloride. Gram.	Correction for sodium nitrate. Gram.	Correction for sodium chloride. Gram.	Molecular weight of sodium nitrate.	Atomic weight of nitrogen.
1.	0.01550	0.01064	....	....	0.01550	0.01066	85.061	14.011
2.	0.20967	0.14419	0.00009	0.00007	0.20976	0.14426	85.061	14.011
3.	6.26217	0.18029	0.00012	0.00009	0.26229	0.18038	85.064	14.014
4.	0.66610	0.46805	0.00035	0.00024	0.66645	0.45829	85.064	14.014
5.	0.93676	0.64422	0.00042	0.00034	0.93718	0.64456	85.058	14.008

Atomic weight of nitrogen = 14.0116 ± 0.000741.

Atomic values used were

Oxygen	16.00
Sodium	23.05
Chlorine	35.45
Specific gravity sodium chloride	2.16
Specific gravity sodium nitrate	2.26

When these results are compared with those obtained by Penny and Stas by treatment of potassium chloride with nitric acid, and the treatment of potassium nitrate with hydrochloric acid (likewise for sodium), a close comparison can be made.

Penny.		Hydrogen chloride method.	
For potassium nitrate	13.9774	For potassium nitrate	14.0118
" sodium nitrate	13.9906	" sodium nitrate	14.0116

Showing a difference of

0.0344 for potassium salt,
0.0210 for sodium salt.

When a mean of the above results is taken, the atomic weight of nitrogen equals

13.9996 for potassium salt,
14.0011 for sodium salt.

Taking now a mean of these values, the atomic weight of nitrogen would be 14.0003.

C.—THE ATOMIC WEIGHT OF ARSENIC.

The atomic weight of arsenic has been obtained from the chloride ($AsCl_3$), the bromide ($AsBr_3$), and the trioxide (As_2O_3).

Pelouze, in 1845,[1] and Dumas, in 1859, determined it by the titration with known quantities of pure silver in the analysis of arsenic trichloride. The mean of their results, as computed by Clarke, gives the atomic weight of arsenic, 74.829. Wallace[2] makes the same titration with silver in the analysis of arsenic tribromide. His value is 74.046. Kessler made a set of determinations by estimating the amount of potassium bichromate required to oxidize 100 parts of arsenic trioxide to arsenic pentoxide. He obtained a mean value of 75.002.

A mean of these results gives the following:

From $AsCl_3$	74 829
" $AsBr_3$	74.046
" As_2O_3	75.002
General mean	74.918

If oxygen = 16, then the atomic weight of arsenic will equal 75.090.

Berzelius, in 1826, heated sulphur and arsenic trioxide together in such a way that sulphur dioxide alone escaped; this method gave 74.840 as the atomic weight of arsenic. But one experiment was made, so that it does not possess much value. In the above method there seems to be a wide variation in the results obtained, the difference between the extreme values is but little less than one unit.

By the hydrogen chloride method, we have but the weighing of the material used in the determination—which must necessarily enter every estimation or analysis—and a single weighing after the action of the acid gas. As in the case of nitrogen, the method seems to be as short and concise as possible.

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[1] *Compt. rend.*, 10, 1047.

[2] Phil. Mag. (4), 18, 279.

The methods and *modus operandi* were exactly the same as those used in the determination of the atomic weight of nitrogen.

The sodium chloride obtained was perfectly white in color. In no instance was it fused. After weighing the salt residue it showed no traces of arsenic, and was readily soluble in cold water without residue. The same conditions of atmosphere were observed.

As the specific gravity of sodium pyroarsenate could not be obtained, it was determined by means of the specific gravity bottle, against chloroform, and was found to be 2.205, while the specific gravity of sodium chloride was taken as 2.16. The atomic values used were:

Oxygen	16.00
Sodium	23.05
Chlorine	35.45

The results here obtained, besides being to a great degree constant, compare favorably with those obtained by Pelouze (74.829) and Kessler (75.002).

A coincidence may here be shown by the fact that the mean of these values gives 74.9155, while the hydrogen chloride method gives 74.9158.

In order to give the method a thorough trial, the amounts taken cover a wide range. The smallest amount used was 0.02176 gram of sodium pyroarsenate, and the largest 3.22485 grams. It will also be noticed that the variation in result is but 0.027 for ten determinations.

No.	Sodium pyroarsenate taken Gram.	Sodium chloride obtained. Gram.	Correction for sodium pyroarsenate. Gram.	Correction for sodium chloride. Gram.	Correction for sodium pyroarsenate. Gram.	Correction for sodium chloride. Gram.	Molecular weight of sodium pyroarsenate.	Atomic weight of arsenic.
1.	0.02176	0.01439	0.00001	0.00000	0.02177	0.01439	354.008	74.904
2.	0.04711	0.03114	0.00002	0.00001	0.04713	0.03115	354.042	74.921
3.	0.05792	0.03828	0.00003	0.00002	0.05795	0.03830	354.054	74.927
4.	0.40780	0.26970	0.00021	0.00011	0.40801	0.26981	354.002	74.901
5.	0.50440	0.33028	0.00026	0.00017	0.50466	0.33045	354.033	74.916
6.	0.77497	0.51222	0.00041	0.00027	0.77538	0.51249	354.034	74.917
7.	0.82853	0.54762	0.00044	0.00029	0.82897	0.54791	354.034	74.917
8.	1.19068	0.78690	0.00056	0.00041	1.19124	0.78731	354.053	74.926
9.	1.67464	1.10681	0.00081	0.00051	1.67545	1.10732	354.057	74.928
10.	3.22485	2.13168	0.00152	0.00099	3.22637	2.13267	354.002	74.901

Atomic weight of arsenic = 74.9158 ± 0.00222.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No 16.]

THE SEPARATION OF VANADIUM FROM ARSENIC.

BY CHARLES FIELD, 3RD, AND EDGAR F. SMITH.

Received October 2, 1896.

AS vanadium and arsenic occur associated in minerals and likewise in artificial products, their separation becomes a matter of consequence.

The course usually pursued in carrying out this separation is that long since recommended for the removal of vanadic acid from its solutions; namely, its precipitation as ammonium metavanadate. Other methods have recently appeared in the literature bearing on analysis. Reference is here made especially to the publication of Fischer.[1]

Experiments made in this laboratory on the behavior of vanadates[2] and arsenates[3] heated in an atmosphere of hydrochloric acid gas, in which both acids were volatilized, suggested the thought that if the sulphides of vanadium and arsenic were exposed to the same vapors perhaps they would show a variation in deportment. And so it has proved. Perfectly dry arsenic trisulphide, previously washed with alcohol, carbon disulphide, and ether, then dried at 100° C., when exposed in a porcelain boat, placed in a combustion tube, was almost completely expelled from the retaining vessel at the ordinary temperature. The last traces were driven out at a temperature little above 150° C. Brown vanadium sulphide, in a perfectly dry condition, treated in the same manner, was not altered. It only remained then to prepare mixtures of known amounts of the two sulphides and subject them to the action of the acid vapor. To this end the following experiments were made:

I. 0.1303 gram of vanadium sulphide,
0.1302 gram of arsenic sulphide.

The arsenic sulphide was volatilized without difficulty and left 0.1297 gram of vanadium sulphide.

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[1] Bestimmung von Vanadinsäure: Dissertation, Rostock, 1894.

[2] *J. Am. Chem. Soc.*, 16, 578.

[3] *Ibid.*, 17, 682.

II. 0.1290 gram of vanadium sulphide,
0.2242 gram of arsenic sulphide,

gave after exposure of one hour to hydrochloric acid vapor a residue of vanadium sulphide, weighing 0.1297 gram.

III. 0.0828 gram of vanadium sulphide,
0.0582 gram of arsenic sulphide,

left 0.0827 gram of vanadium sulphide.

IV. 0.1306 gram of vanadium sulphide,
0.2028 gram of arsenic sulphide,

gave a residue of 0.1308 gram of vanadium sulphide.

V. 0.1403 gram of vanadium sulphide,
0.2409 gram of arsenic sulphide,

left 0.1404 gram of vanadium sulphide.

The temperature in these experiments was not allowed to exceed 250° C., as beyond that point there is danger of affecting the vanadium and causing its partial volatilization.

The method worked so well and with such evidently favorable results that the following course was adopted in the analysis of a specimen of the mineral vanadinite. 0.2500 gram of air-dried and finely divided material was placed in a porcelain boat; the latter was then introduced into a combustion tube and gently heated in a current of dry hydrochloric acid gas. By this treatment vanadic and arsenic oxides were expelled, leaving lead phosphate and chloride. The receiver containing the vanadium and arsenic was made alkaline and digested with ammonium sulphide. From the solution of the sulpho-salts the vanadium and arsenic sulphides were set free by a dilute acid. After washing and careful drying these sulphides were separated as indicated in the preceding lines, then changed to oxides and determined in the usual manner. The sum of the total constituents determined as lead oxide, phosphoric oxide, vanadic and arsenic oxides, with some lead chloride, amounted to 0.2501 gram.

The method in addition to being satisfactory in the analytical way, certainly forms a very excellent means of purifying and freeing vanadium from arsenic.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 17.]

THE SEPARATION OF MANGANESE FROM TUNGSTIC ACID.

BY WALTER T. TAGGART AND EDGAR F. SMITH.

Received October 2, 1896.

THE necessity of obtaining pure tungstic acid from time to time, using wolframite as the starting out material, has frequently suggested the inquiry as to what course would probably prove the best in the quantitative separation of this acid from oxides, such as those of iron and manganese.

In the experiments recorded in this communication only the results obtained from a study of mixtures of a manganous salt and a soluble alkali tungstate will be given. The directions taken in the experimentation were, 1st, to effect the separation by the use of yellow ammonium sulphide in the presence of ammonium chloride; 2nd, to eliminate the acid oxide by the use of an alkaline carbonate.

Following the first course, mixtures of definite amounts of ammonium tungstate and manganous chloride were made. To these was added water and a considerable excess of yellow ammonium sulphide, together with ammonium chloride. The mixtures were digested on a water-bath at 70° C., for several hours, and the vessels containing them were then closed and allowed to stand during the night. The manganese sulphide was filtered out, and, after solution, was changed into sulphate and weighed as such, or it was finally obtained as protosesquioxide in the customary way.

RESULTS.

Manganous oxide present. Gram.	Manganous oxide found. Gram.
0.1950	0.2121
0.1949	0.2255
0.1290	0.1708
0.1287	0.1720
0.1291	0.1760

In every trial tungstic acid adhered to the metallic oxide.

In trying the second suggestion the soluble tungstate and the soluble manganous salt were digested for some hours in a platinum dish, upon a water-bath, with an excess of a ten per cent. potassium carbonate solution, after which the whole was evaporated to dryness, the residue boiled up with water, the manganous carbonate filtered out, washed, and finally converted into protosesquioxide.

RESULTS.

Manganous oxide present. Gram.	Manganous oxide found. Gram.
0.1949	0.1516
0.1949	0.1534

Several trial were made using a fifty per cent. solution of potassium carbonate.

RESULTS.

Manganous oxide present. Gram.	Manganous oxide found. Gram.
0.1951	0.1745
0.1950	0.1528

The experimental evidence given in the preceding paragraphs leaves no doubt as to the insufficiency of the two methods, which were tried, in effecting the desired separation. It is probable that fusion with an alkaline carbonate will alone answer for this purpose. How complete that course would be can only be ascertained by careful experimentation.

In the course of analysis molybdenum is quite often obtained as sulphide. Its conversion into a weighable form is attended with more or less difficulty. Trials made in connection with its estimation show that if the sulphide, as generally obtained, be dried, then intimately mixed with anhydrous oxalic acid, its careful ignition to trioxide can be made quite rapidly.

RESULTS.

Molybdenum trioxide taken. Gram.	Molybdenum trioxide found. Gram.
0.3000	0.3009
0.3000	0.2990
0.1007	0.1011

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 18.]

THE SEPARATION OF BISMUTH FROM LEAD.

BY ARTHUR L. BENKERT AND EDGAR F. SMITH.

Received October 2, 1896.

MANY methods have been suggested to effect this separation. In a recent issue of the *Zeitschrift für angewandte Chemie* (1895, p. 530), Olav Steen reviews thirteen of these methods and concludes that an early proposal of Rose,[1] in which the lead is thrown out as chloride and weighed as sulphate, another by Löwe,[2] in which the bismuth is removed as basic nitrate, and a late suggestion made by Jannasch,[3] *viz.*, the expulsion of the bismuth as bromide from a mixture of lead and bismuth sulphides by an air current carrying bromine are the most satisfactory. At least these methods gave Steen the best results. The separation of bismuth from lead frequently confronts the analyst, and any novelty in this direction cannot be absolutely devoid of interest, hence the present communication, which brings data that may perhaps prove of service in the hands of others who are interested in the solution of this analytical problem.

It will be recalled that Herzog[4] proposed to separate bismuth from lead by precipitating the former as basic acetate. The method required considerable time for execution, and in other hands than those of its author apparently has not yielded entirely satisfactory results.

An idea closely related to that of Herzog would be the substitution of a formate solution for that of the acetate. This was done with results that are very interesting.

Solutions of lead nitrate and bismuth nitrate in nitric acid were made up of such strength that twenty cc. of the first contained 0.2076 gram of lead oxide, and twenty cc. of the second 0.1800 gram of bismuth trioxide. The lead and bismuth were accurately determined after dilution to a liter. Twenty cc. of these two nitrate solutions were then introduced into a beaker

[1] *Ann. chem. phys. Pogg.*, 110, 425.

[2] *J. prakt. Chem.*, 74, 348.

[3] *Ber. d. chem. Ges.*, 25, 124.

[4] *Ztschr. anal. Chem.*, 27, 650.

glass, carefully diluted and almost neutralized with sodium carbonate, or until the incipient precipitate dissolved slowly, when considerable sodium formate solution of sp. gr. 1.084 and a few drops of aqueous formic acid were added. The total dilution of the liquid was 250 cc. It was gradually heated to boiling and held at that point for *five* minutes. The precipitate was then allowed to subside, but was filtered while yet hot. The basic formate separates rapidly and is easily washed if not boiled too long. It was washed with hot water, then dissolved in dilute nitric acid and precipitated with ammonium carbonate. The ignited bismuth trioxide weighed too much; it contained lead. However, the impure oxide was dissolved in nitric acid, diluted to 250 cc., and after the addition of sodium carbonate to almost complete neutralization, sodium formate and free formic acid were added as before, and *the precipitation of basic formate repeated*. This precipitate after solution and the bismuth thrown out by ammonium carbonate gave 0.1804 gram of bismuth oxide instead of 0.1800 gram as required by theory. Seven additional separations, in which the quantities of bismuth and lead were the same as indicated above, gave:

0.1806 gram of Bi_2O_3.
0.1806 " " "
0.1803 " " "
0.1804 " " "
0.1804 " " "
0.1805 " " "
0.1796 " " "

The conditions in these determinations were similar to those previously outlined.

With a solution containing 0.3600 gram of bismuth oxide and 0.2076 gram of lead oxide, operating in an analogous manner, two results were obtained:

0.3595 gram of Bi_2O_3.
0.3605 " " "

instead of the required 0.3600 gram.

The residual bismuth trioxide was examined for lead, but none was found.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

XLVIII.—ON SOME NEW FORMS OF GAS GENERATORS.[1]

BY THOMAS H. NORTON.

Received August 27, 1896.

IMPROVEMENTS in the construction of the automatic generators, for the gases most frequently used in our laboratories, are always welcome. The following three types, which I devised some time since, have been subjected to prolonged trial in the laboratory of the University, and have given such satisfactory results, that a detailed description would seem worthy of publication.

In Fig. 1 is represented a gas generator for hydrogen, hydrogen sulphide, etc., which differs in several details from well known types of the same general outline. It is constructed of glazed earthenware, and is easily made in our ordinary potteries. *A*, the outside container, is provided with handles on the outside, and is ordinarily sixty cm. in height. Its chief peculiarity is the presence on opposite sides of the inner wall, of the shoulders *DD*, each about four cm. wide and slightly concave on the lower surface. *B*, the gas reservoir, is of the ordinary bell-jar construction, with orifice at the top for the introduction of a perforated stopper and outlet tube. It is provided with projecting shoulders three cm. wide, corresponding to *DD*, and at such a height that they barely slip beneath the latter. At the bottom are frequent circular perforations, one centimeter in diameter, to allow of the easy passage of the acid charge. The recipient *C*, designed to hold zinc or any solid charge, is provided with a loose disk perforated with many fine openings and resting upon the shoulder of the constriction. Beneath the constriction are perforations corresponding to those in *B*. A strong copper wire or rod, passing through the perforations of both parts of the apparatus, holds *B* and *C* in their mutual position to each other.

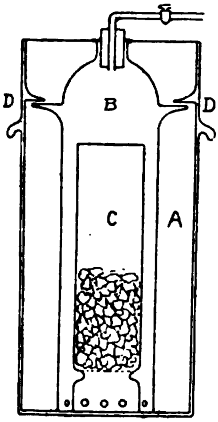

FIG. 1.

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[1] Read before the American Association for the Advancement of Science at the Buffalo Meeting.

The working of the generator is exceedingly simple. *C* receives its charge of zinc, marble or ferrous sulphide. *B* is placed over it. The copper rod is passed through the perforations at the bottom. *B* with *C* is then introduced into *A*, and turned until the shoulders of *B* are beneath *DD*. *A* is then filled with the acid charge. The buoyancy of *B* is partly overcome by the rigid attachment of *C*, and entirely prevented by *DD*. Gas can be drawn off as desired, by opening the tap at the outlet tube. When, as naturally occurs, the acid in the lower portion of the generator becomes weak and the evolution of gas sluggish, the exit tap is closed, *B* is turned slightly so as to be free from *DD*, and is then lifted, by grasping the neck, along with the holder *C*, until entirely above the surface of the acid. Both are then plunged to the bottom of *A*, and a few repetitions of this churning movement renders the acid charge of uniform strength.

This style of generator has rendered excellent service. For example, one sixty centimeters in height easily supplies all the hydrogen sulphide required by a class of thirty in qualitative analysis. The special advantages of this generator are to be found in the ease and simplicity with which the buoyancy of the gas reservoir is overcome and the acid charge is maintained at a uniform strength until practically exhausted.

In Fig. 2 we have a less compact and less transportable form, but one which maintains the uniform strength of the acid charge until it is exhausted, without the need of special manipulation, as described above. It is particularly designed for use where small amounts of hydrogen sulphide are in constant requisition, as in the laboratory for qualitative analysis, and it has the advantage of being capable of easy construction from the glassware found in any well equipped laboratory. *A* is a capacious tubulated bell-jar inverted and resting upon

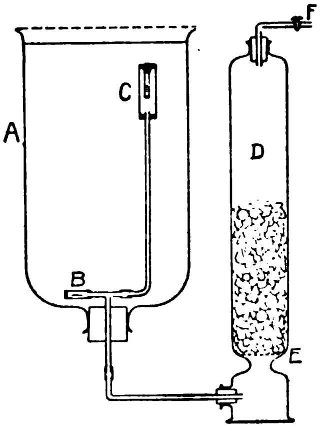


FIG. 2.

either a tripod or the ring of an ordinary support. The perforated stopper in the neck is traversed by a T tube. One terminal of this tube is connected with a simple Bunsen valve, *B*, *i. e.*, a piece of rubber tubing, closed at one end and provided with a clean cut slit in the rubber some two cm. in length. The other terminal of the T tube is connected with *C* in the upper portion of *A*. The attachment *C* is similar to that frequently introduced between suction pumps and filtering flasks. It is the reverse of *B* in its construction, allowing a current of liquid to enter from the outside through the rubber valve. *A* serves as a reservoir for the acid charge. The third external terminal of the T tube is connected with the tubulus of the lower portion of an ordinary lime drying tower, *D*, preferably of the largest size constructed. *D* serves as the recipient for the ferrous sulphide, etc., which may be used, and is provided with a perforated disk at *E* and the outlet tube *F*, the latter on a level with the top of *A*. The working of the generator is exceedingly simple. *A* is charged with acid and *D* with, say, ferrous sulphide. When *F* is opened the acid flows through *C* into *D*. When *F* is closed the pressure of the gas evolved forces the acid back into *A* through *B*. The result is that the supply of acid furnished *D* is always from the top of the reservoir *A*, and hence stronger than that found in the lower strata, which are successively of greater specific gravity, weaker in acid and richer in saline matter, as the bottom is approached. The arrangement permits of a very complete utilization of the acid. When the current of gas is in continuous demand, and evolution becomes sluggish, it is necessary to close the tap at *F* for a short time until the liquid in *D* is driven back into *A*.

Care must be exercised in constructing the valve at *C*, so that it will yield to a very slight pressure. To effect this the slit in the rubber should be at least two cm. in length. When the apparatus is used exclusively for the evolution of hydrogen sulphide to be employed in qualitative analysis, it is desirable to have beyond *F* some device which regulates uniformly the strength of the current of gas and keeps it within the limits of easy absorption. In practice this has been accomplished most simply by introducing into the rubber tube attached to *F* a short piece of glass tubing, one end of which is drawn out so as to form a very narrow opening.

Essentially the same principle for the control of the strength of the acid charge is to be found in the generator devised recently by Professor Harris. In consequence of the costly character of the latter, due largely to the use of valves of elaborate construction, the form of generator just described may be welcome to many on account of its simplicity and inexpensiveness.

An automatic chlorine generator based upon the use of manganese dioxide, has long been desired. In Fig. 3 is shown such a generator which for six years has rendered satisfactory service, both on the lecture table and in the laboratory. The essential parts only are outlined without the accompanying supports. *A* is a copper funnel, provided with a hollow projection *C*, on one side, perfectly similar in make to the funnels used for hot water filtration. It can be advantageously replaced by the more graceful and modern type of aluminum funnel, resting in a ring burner. The reservoir *B* is of glass, and is an article of current manufacture, obtainable from all dealers in chemical glassware. The long, tapering neck is tightly fastened in the neck of the funnel by means of a section of rubber tubing. A large opening at the top, closed by a rubber stopper, serves for the admission of the charge. In a smaller tubulure on the side is a perforated rubber stopper with outlet tube and tap. The funnel with its reservoir is held firmly in a support, so that the end of *C* is about two cm. above the top of an ordinary burner. A perforated plate is introduced into *B* so as to prevent solid matter from falling into the narrow neck. The latter is connected at *D* with a large tubulated bottle *E*, which serves as a reservoir for hydrochloric acid, and is attached to a support so that it can be raised

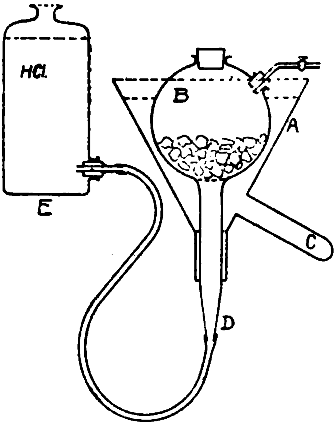


FIG. 3.

or lowered at will. When in use *B* is filled to two-thirds of its capacity with manganese dioxide, large lumps alone being used, as powdered mineral may easily cause a stoppage of the connections. *E* is filled with hydrochloric acid and raised to a level slightly above the top of *B*. Water is poured into the funnel *A* until it is nearly full, and a lamp is placed under *C*. As soon as the temperature has reached about 80°, a very small flame suffices to maintain the activity of the generator. When the exit from *B* is open, the acid enters and the evolution of chlorine continues until checked by closing the tap, when the acid is driven back into *E*. A slight agitation of the latter before opening the tap serves to prevent the accumulation of a stratum of weak acid at the bottom. It is advisable to lower the reservoir *E* when a current is not required, so as to avoid pressure and any possible escape through minute leaks. In practice it is also found desirable to connect the opening of *E* by a flexible tube with a bottle of caustic soda solution, the tube terminating at the surface of the solution. This prevents any escape into the surrounding air of chlorine, with which the contents of *E* are soon saturated. When thus arranged a current of the gas can be taken at will from the generator, the sole condition being the maintenance of a small flame beneath *C*. The manifold advantages of such a device, especially for the lecture table, will be appreciated by all who attempt an extended series of experiments with chlorine. As described above the generator can be readily constructed from pieces of apparatus ordinarily found in a well equipped laboratory. I have found a generator in which the reservoir *B* contains 1500 cc., a very convenient size for use in the lecture room.

MINERAL CONSTITUENTS OF THE WATERMELON.

By George F. Payne.

Received September 28, 1896.

THE watermelon is not a crop that is widely grown even in this country with great success. It is this very reason which makes it a desirable crop to handle in Georgia, as the watermelons in this state attain finer flavor, crispness, juiciness and sweetness than anywhere else in the world.

Upon analysis of two medium-sized watermelons cut up and mixed together, we found them to contain just one-third per cent. of pure ash, calculated as free from carbonic acid. The exact figures were 0.3338, which in our calculations we will round off into an even one-third, which it practically is.

The composition of watermelon ash is as follows:

	Per cent.
Sulphur trioxide	4.41
Calcium oxide	5.54
Magnesium oxide	6.74
Potassium oxide	61.18
Sodium oxide	4.31
Silicon dioxide	2.15
Phosphorus pentoxide	10.25
Chlorine	4.94
Iron sesquioxide	0.48
Total	100.00

A good average crop of watermelons is considered to be about one-half carload to the acre, though much larger crops than this are sometimes made. Large watermelons are also considered desirable, hence in considering what is carried off from the land by the removal of the crop, it is well to consider how much would be taken off by a large crop, as it is the large crops which we desire to produce. We have before us a report of a crop of watermelons upon an acre of land which is an unusually large one, but which was weighed up in the presence of disinterested witnesses and sworn to by them as being honestly grown upon an acre and correctly weighed. This crop weighed 39,766 pounds. One-third per cent. of such a crop would be pure ash, and consequently the mineral plant food taken out of an acre of land by such a crop would be as follows:

	Pounds.
Sulphur trioxide	5.85
Calcium oxide	7.34
Magnesium oxide	8.93
Potassium oxide	81.09
Sodium oxide	5.71
Silicon dioxide	2.85
Phosphorus pentoxide	13.59
Chlorine	6.55
Iron sesquioxide	0.64
Total	132.55

In the crop mentioned above to replace the phosphoric acid and potash carried off from one acre by the melons alone, not taking into account the vines and roots, would require:

	Pounds.
Acid phosphate (thirteen per cent. P_2O_5)	100
Muriate of potash (fifty per cent. K_2O)	160

A fair crop of melons upon good land, however, is usually considered to be about one-third of the above large crop or about one-half carload. If we estimate then the amounts of phosphoric acid and potash required for an average crop of fair character, such a crop will take from the soil materials to replace which will require about:

	Pounds.
Acid phosphate	33⅓
Muriate of potash	53⅓

This will give about four and one-half pounds of available phosphoric acid to an acre, and about twenty-seven pounds of pure potash to an acre. The usual goods on the market guarantee about ten per cent. of available phosphoric acid and about one per cent. of potash. The use of 300 pounds of such goods upon each acre of watermelons, furnishes thirty pounds of available phosphoric acid, or about six and one-half times as much as is needed to replace what is carried off by the watermelons. It also furnishes about three pounds of potash, which is only one-ninth of what is carried off by the crop removed. This being the case it shows with what advantage and economy the watermelon grower can replace a large proportion of his phosphoric acid with potash.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 22.]

A MODIFIED FORM OF THE EBULLIOSCOPE.

BY H. W. WILEY.

Received September 26, 1896.

THE determination of the alcohol in wines and beers, from the temperature of the vapors given off on boiling at atmospheric pressures, has long been practiced. The instrument by means of which this determination is made is known as the ebullioscope or ebulliometer. The use of this instrument was proposed many years ago by Tabarié, and it has been improved by Malligand, Salleron and others.

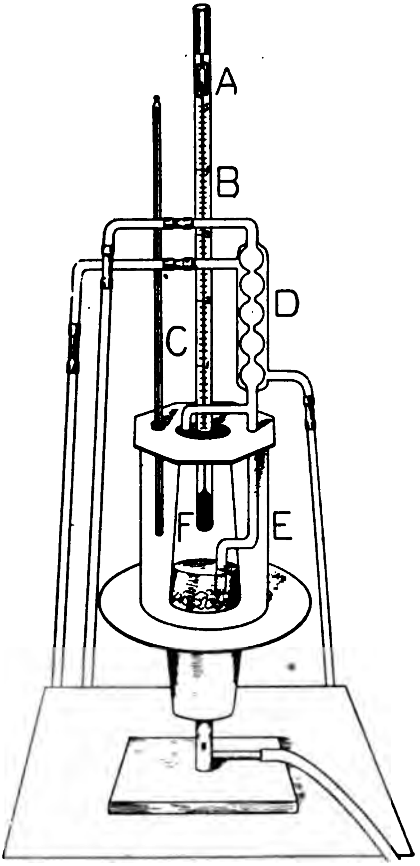
It is evident that if so simple an apparatus could be made to give accurate data, it would come into general use for ordinary purposes. The difficulties which have attended the use of the ebullioscope, however, have been of such a nature as to render the data given by it somewhat unreliable. Among these difficulties may be mentioned the fact that a wine or beer contains a considerable quantity of dissolved matters, which serve to render the temperature of the boiling liquid higher than the temperature of a mixture of a similar percentage of alcohol with water. While the temperature of the vapors emitted are, theoretically, not influenced in a marked degree by the initial temperature at which they are formed, nevertheless, in practice it has been shown that the tendency of the higher initial boiling point is to give a higher reading to the thermometer whose bulb is surrounded by the emitted vapors.

Another difficulty attending the use of the ebullioscope is found in the fact that the percentage of alcohol in the vapors emitted is much greater than in the residual liquid. As a result, it is difficult to establish a balance between the condensed vapors and the liquid remaining in the flask, in such a manner as to secure a continuous evolution of a vapor containing a definite proportion of alcohol.

In the third place, it has been customary to return the condensed vapors through the apparatus in such a way that they come in contact with the uncondensed vapors surrounding the thermometer. By this means the vapors surrounding the bulb of the thermometer are subjected to changes of temperature which render it difficult to get a mean reading of the height of the mercurial column in the instrument. The variations which the mercurial column may undergo amount, in some instances, to two or three-tenths of a degree and as each tenth of a degree represents approximately a tenth of a per cent. of alcohol, it is not difficult to see that these variations would tend to lead to erroneous results.

In the fourth place, barometric changes, which are constantly taking place in the atmosphere, change the boiling point of the vapor of water so that it is frequently necessary to check the instrument with pure water, in order to have an initial temperature for the calculations.

In the apparatus which is presented, an effort has been made to remedy the difficulties which have been mentioned above. The apparatus consists of the flask *F*, which is closed by a rubber stopper carrying the large thermometer *B* and a tube leading to the condenser *D*. The vapors which are given off during ebullition are condensed in *D* and return to the flask through the tube, as indicated in the figure, entering the flask below the surface of the liquid therein.



The flask is heated by a gas lamp and is placed upon a circular disk of asbestos in such a way as to entirely cover the hole in the center of the asbestos disk, which is a little smaller than the bottom of the flask. The whole apparatus is protected from external influences of temperature by the glass cylinder *E*, which rests upon the asbestos disk below and is covered with a detachable, stiff rubber cloth disk above.

The thermometer *C* indicates the temperature of the ambient air between *F* and *E*. The reading of the thermometer *B* should always be made at a given temperature of the ambient air, as indicated by *C*. The tube leading from the top of the condenser *D* to the left, is made long and is left open at its lower extremity, in order to secure atmospheric pressure in *F*, and at the same time prevent the diffusion of the alcohol vapors through *D*.

The flame of the lamp is so regulated as to bring the temperature of the thermometer *C* to about 90° in ten minutes for substances not containing over five per cent. of alcohol. After boiling for a few minutes, the temperature, as indicated in the thermometer *B*, is constant, and the readings of the thermometer should be made at intervals of about half a minute for two minutes. Some pieces of scrap platinum placed in the flask will prevent bumping and secure a more uniform evolution of vapor.

Slight variations, due to the changes in temperature of the vapor, are thus reduced to a minimum effect upon the final results.

The apparatus is easily operated, is quickly charged and discharged and with it at least three determinations of alcohol can be made in an hour.

The thermometer used is the same as is employed for the determination of freezing and boiling points in the ascertainment of molecular weights. The reading of the thermometer is arbitrary, but the degrees indicated are centigrade. The thermometer is set in the first place by putting the bulb in water containing sixteen grams of common salt to 100 cc. When the water is fully boiling, the excess of mercury is removed from the column in the receptacle at the top and then, on placing in ordinary boiling water, the column of mercury will be found a little above the 5° mark. This will allow a variation in all of 5° in the temperature, and a thermometer thus set can be used for the estimation of percentages of alcohol from one to five and a half, by volume. When the liquor contains a larger percentage of alcohol than this, it is advisable to dilute it until it reaches the standard mentioned.

In order to avoid frequent checking of the thermometer, rendered necessary by changes in barometric pressure, I use a second apparatus made exactly as the one described, in which water is kept constantly boiling. It is only necessary in this case to read the two thermometers at the same instant in order to make any necessary correction required by changes in barometric pressure.

It is not my purpose here to submit a table showing the percentages of alcohol corresponding to any given depression in the temperature of the boiling vapor. It is only necessary to call attention to the fact that for the percentages named, the platted line showing the variation in depression from 0° to five per cent. by volume of alcohol is practically straight and that for each 0.8° change in the boiling point of the vapor, there is a change of about one per cent by volume of alcohol. This rule can be safely applied for practical purposes to all liquors containing not more than five and five-tenths per cent. of alcohol. For instance, if, in a given case, the temperature of the vapor of boiling water, as marked by the thermometer, is 5.155°, and the temperature of the vapor of a sample of beer is 2.345°, the depression is equivalent to 2.810°, and the percentage of alcohol by volume is therefore 2.81 divided by 0.80 = 3.51.

The thermometer used is graduated to hundredths of a degree and is read by means of a cathetometer, which will easily give readings to five thousandths of a degree.

The reading of the thermometer is facilitated by covering the bulb with a test-tube containing water. The high specific heat of the water distributes evenly any little variations of temperature which otherwise would cause the mercurial column in thermometer *B* to oscillate. The water jacket also serves as a protection against the projection of any particles of the boiling liquor directly against the bulb of the thermometer.

It is believed that this apparatus is the best form of ebullioscope which has yet been offered for practical use to analysts.

VOLUMETRIC DETERMINATION OF ACETONE.[1]

BY EDWARD R. SQUIBB.

Received November 9, 1896.

IN the *Moniteur Scientifique* of 1893, 41, 4 Serie, Vol. 7, 1°, p. 272–274, MM. J. Robineau and G. Rollin publish a paper entitled, "Dosage Volumetrique de L'Acetone," and the following is, first, a free translation and abridgement of this paper; and second, the detail of an improvement of the process whereby it is rendered easier, more simple, quicker, and better adapted to technical uses, whilst still sufficiently accurate for most purposes.

FIRST, FREE TRANSLATION.

The common way of determining the proportion of acetone in a liquid containing it is to convert the acetone into iodoform by means of iodine in the presence of soda after eliminating from the liquid everything that would interfere with the proper reaction.

For this process binormal solutions of iodine and of sodium hydroxide are used, and the precipitated iodoform is washed, dried, and weighed, or is dissolved in ether, and the whole or a fraction of the ethereal solution is dried over sulphuric acid and weighed.

The appreciable volatility of iodoform at ordinary temperatures introduces a source of error that is objectionable, especially when dealing with small quantities.

But, aside from this, the time required for this process is relatively so long that we have sought to change it to a volumetric process that is more rapid.

Our proceeding consists in mixing the acetone with a solution of potassium iodide and sodium hydroxide, and then transforming it into iodoform with a titrated solution of a hypochlorite. The end reaction is indicated by the appearance of a blue color, when a drop of the liquid is touched with a drop of bicarbonated starch solution.

From the quantity of hypochlorite used the quantity of acetone is deduced.

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[1] Read before the New York Section of the American Chemical Society, November 6th, 1896.

For it happens that the presence of even the smallest trace of an alkaline hypoiodite, in a solution of soda, gives a blue color with a starch solution which contains an excess of sodium bicarbonate.

Again, a liquid containing acetone, an iodide and caustic soda in excess, and into which a solution of hypochlorite is passed, gives no reaction with bicarbonated starch until the whole of the acetone is converted into iodoform.

This proceeding, however, only gives constant results when certain precautions are taken. Unless the liquid containing the acetone be sufficiently alkaline, an excess of hypochlorite will be required to decompose all the acetone.

The potassium iodide must be in excess.

The dilution must be fairly uniform, and the concentration of the hypochlorite about the same for the different titrations.

The process should not be used in too strong a light.

It is very important that the liquid should be constantly stirred during the additions of the hypochlorite.

The strength of the hypochlorite solution is ascertained by trial against a pure acetone made by the bisulphite process.

PREPARATION OF THE HYPOCHLORITE.

For the titration of liquids containing considerable proportions of acetone, the hypochlorite solution is prepared as follows:

To 500 cc. of the concentrated solution of sodium hypochlorite of commerce, which tests from forty-five to fifty-five volumes of chlorine, an equal measure of water, and ten cc. of solution of pure soda of 36° B., are added, and the solution is kept in an amber colored bottle, well corked.

TITRATION OF THE HYPOCHLORITE SOLUTION.

About two grams of pure acetone from bisulphite is weighed off and diluted to 500 cc.

Then ten grams of pure potassium iodide is put into a conical Bohemian beaker and 100 cc. of the diluted acetone and twenty cc. of solution of caustic soda of 28° B. are successively added, and the whole is stirred until the iodide is dissolved and the liquid is homogeneous.

Into this the hypochlorite solution is passed drop by drop from a burette, with constant stirring, precipitating the iodoform in large flakes which easily settle out. When farther additions of the hypochlorite give but a light cloudiness a drop of the liquid is transferred to a white porcelain plate by means of a glass rod and is there brought in contact with a drop of the bicarbonated starch solution. As soon as the hypochlorite is in excess the blue color appears very distinctly. The volume of hypochlorite used is then read off from the burette, and then for security of result the titration is repeated.

Example.—2.081 grams pure acetone is weighed off and diluted to 500 cc; 100 cc. of this solution requires 22.5 cc. of the hypochlorite. This gives for each cc. of hypochlorite 0.01874 gram of pure acetone. These results are liable to vary a little if the conditions of the experiment vary much. The stirring is supposed to be constant, and the hypochlorite solution to be regularly added.

If to 100 cc. of the diluted acetone 100 cc. of water be added and the same quantities of iodide and soda as above, 22.05 cc. of hypochlorite is required instead of 22.5 cc. In using forty cc. of the soda solution instead of twenty cc., twenty-two cc. of the hypochlorite is required. In using sixty cc. of soda solution instead of twenty cc., 21.6 cc. of the hypochlorite is required. In using ten cc. of soda instead of twenty cc., twenty-three cc. of the hypochlorite is required.

These results show that dilution of the acetone and a small excess of soda have but little influence, but that a deficiency in alkalinity has a very considerable effect on the quantity of hypochlorite required. And farther, that the alkalinity indicated by twenty cc. of soda solution of 28° B. appears to be normal.

Under the given conditions of alkalinity and dilution the relations between acetone and the available chlorine of the hypochlorite is obviously one molecule of acetone to six atoms of chlorine.

The solution of hypochlorite used by us was the liquor of Penot, testing 21.56 volumes.

The titration of the hypochlorite with pure acetone may be omitted, simply determining the available chlorine of the liquor of Penot instead, but we prefer the titration with pure acetone.

DETERMINATION OF ACETONE IN A COMPLEX LIQUID.

We give as an example of this the titration of a complex liquid made with precision, which liquid has served us to control the accuracy of the process.

The complex liquid contained :

1.510 grams water,
1.677 " ethyl alcohol,
1.550 " methyl alcohol, pure
3.149 " acetone, pure from bisulphite
} 39.98 per cent. acetone.

Of this mixture 3.2445 grams was weighed off and diluted to 500 cc. Proceeding as before 100 cc. of this dilution, ten grams of potassium iodide, and twenty cc. of soda solution of 28° B. required 13.85 cc. of the hypochlorite. This by calculation gives 39.99 per cent. of acetone, and thus verifies the composition of the complex liquid; and it is seen that the presence of ethyl alcohol is without influence on the result.

The effect of the presence of paraldehyde in the same complex liquid was tried by a similar titration.

To 100 cc. of the complex solution corresponding to 0.4162 gram of pure acetone, ten cc. of an aqueous solution containing five per cent. of pure paraldehyde was added (say one-half gram) or a little more paraldehyde than acetone. This mixture took 22.4 cc. of the hypochlorite instead of 22.2 cc. as required.

This variation is slight for the relatively large proportion of paraldehyde, and is greater for larger proportions, but instances are rare in which paraldehyde is present in such proportions.

In all such instances where the presence of the aldehyde has been established by the process of Bardy, the acetone should be purified by this process before titration.

For the determination of acetone in very dilute solutions a solution of hypochlorite of one-fifth of the above strength is preferred. That is, a solution containing four or five volumes of available chlorine, and the degree of alkalinity should be proportionately reduced.

With a little practice it is easy to judge as to how much acetone is present in a liquid to be titrated, and from this to judge of the corresponding quantity of hypochlorite required, and in this way keep the conditions of the method nearly uniform, and the more uniform the conditions the more constant the results.

This process has the great advantage of being rapid, and thus of permitting a number of titrations being made in a short time with results sufficiently accurate.

REMARKS.

The reaction used in this titration is very delicate, and where traces of acetone are concerned it is better seen when there is excess of iodide and of soda and but little hypochlorite. An aqueous solution of 0.004 gram of acetone in the liter gives a heavy cloudiness immediately. The reaction with 0.0012 gram of acetone in the liter is seen in a few moments. With 0.0008 gram to the liter the reaction is difficult to see. This reaction should not be made in a bright light. In sunshine or in a very bright light the traces of iodoform produced disappear very rapidly, the liquid becoming clear, but in a dim light the precipitate does not disappear.

The titrated solution of hypochlorite should be kept in amber-colored glass in a cool place and sheltered from bright light. The titration should be frequently repeated, because it varies rather rapidly, especially when diluted. We have made a series of experiments on this point, which strikingly show these variations under different influences. A solution of hypochlorite prepared for titrations gave 22.16 volumes of available chlorine; kept in a cool place, in obscurity for six days, it gave 21.96; kept in colorless glass, corked, in a bright light, most of the time in sunlight, for seven days, it gave 12.32. In a water-bath at 100° C. for a quarter of an hour it gave, when cooled, 19.48.

END OF TRANSLATION.

The rapidly increasing uses of acetone in the three years that have passed since the publication of this important paper of Robineau and Rollin have given to it so much additional importance that it seemed well to the present writer—who early adopted this volumetric method—to attempt to modify the method in the direction of greater simplicity and rapidity, even if this should be at the cost of a little of its accuracy. As acetone comes more and more to take the place of both ethyl and methyl alcohol as much the better solvent for most purposes, and as its manufacture is cheapened, it becomes more and more desirable to have a rapid and easy way of estimating its proportions in mixtures or under conditions to which specific gravity is not applicable.

Therefore, taking the above quoted paper as a basis, and giving full credit to the authors of it for every important principle and step of the method, the following slight modifications are offered as the result of about three months' experience with the original process and over a year's experience with the modifications.

STANDARD SOLUTION OF ACETONE.

A flask of 100 cc. capacity containing about fifty cc. of distilled water is carefully weighed. To this is added about thirteen cc. of pure acetone, made by the bisulphite process. The weight is then again taken, when it will be found that the acetone added is a fraction more or less than ten grams. The dilution is then transferred to a measuring flask, the weighing flask being rinsed in and is farther diluted with distilled water until each ten cc. of the dilution contains one-tenth gram of acetone. This is kept in a well stoppered bottle of dark glass, for, although the writer has no evidence of any change taking place in acetone, and believes it to be quite as permanent as ethyl alcohol, still it may be well to keep a dilute standard solution protected against bright light.

Of this solution or dilution ten cc. equal to one-tenth gram of acetone, is accurately measured off for each titration of the solution of hypochlorite.

SOLUTION OF POTASSIUM IODIDE.

Of this salt 250 grams are dissolved in distilled water, and the solution is made up to one liter, when each ten cc. will contain two and a half grams of the iodide.

SOLUTION OF SODIUM HYDROXIDE.

Of commercial caustic soda, purified by alcohol, 257 grams is dissolved in distilled water, the solution made up to one liter, and set aside until it settles quite clear. Then 850 cc. of clear solution is poured off and added to the solution of potassium iodide, making 1,850 cc. of total solution.

Of this solution twenty cc. is taken for each titration.

The remainder of the soda solution is again allowed to settle clear for farther use in the hypochlorite solution.

SOLUTION OF SODIUM HYPOCHLORITE.

The officinal solution of chlorinated soda of the U. S. Pharmacopœia ("Liquor Sodæ Chloratæ," U. S. P.) answers very well for this process, the officinal strength of two and six-tenths per cent. of available chlorine being quite convenient.

To a liter of this solution in a bottle of dark glass, twenty-five cc. of the above described clear soda solution is added and the mixture well shaken.

If in buying the "Solution of Chlorinated Soda" of the U. S. P. for this process it should be found, as is not unfrequently the case, weaker than is required by the U. S. P., or, if by keeping it becomes weaker, this will be at once discovered on balancing it against the standard acetone solution, and so long as the one-tenth gram of acetone does not require more than say twenty cc. of the more dilute hypochlorite, the formula need not be modified.

If there be much of this titration to do it is very convenient to fit this bottle with an automatic zero burette,[1] as shown in the following illustration, this form being, so far as is known, original with the writer and very convenient for general rapid working with a burette. The advantage is, beside that of rapid and easy working, that it does not require a special burette and is easily fitted up from the resources of any laboratory.

BICARBONATED STARCH SOLUTION.

Starch, 0.125 gram, is mixed with five cc. of cold water, and then added to twenty cc. of boiling water and boiled. When cold two grams of sodium acid carbonate is added and stirred until dissolved. Kept in a colorless bottle this solution does not sensibly diminish in delicacy or reaction in three months. But for how much longer it would remain good for this reaction was not tried.

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[1] This Journal, 16, 145.

AUTOMATIC ZERO BURETTE.

THE TITRATION.

The burette being filled with the solution of sodium hypochlorite, ten cc. of the standard solution of acetone (equal to one-tenth gram of acetone) is measured into a beaker of about fifty cc. capacity, and twenty cc. of the mixed solution of iodide and soda is added and stirred well. Into this the hypochlorite solution is passed in rapid dropping, with constant stirring, until eight or ten cc. has been run in. Then the precipitated iodoform is allowed to settle out, and a drop or two more hypochlorite is added. Should this produce a dense cloudiness one-half cc. more hypochlorite is added, and well stirred and again allowed to settle. Then a drop or two more of hypochlorite is added. If there should still be a cloudiness, another one-half cc. of the hypochlorite is added and well stirred, and so on until the cloudiness is very slight. Then the starch testing begins.

A small drop of the liquid is transferred by a rod to a white porcelain tile or plate, and a similar small drop of the starch solution is placed very near it. Then with the first rod the drops are made to connect by a fine line, so that the whole has a dumb-bell form. If there be no blue color, one or two-tenths cc. more of the hypochlorite is added and well stirred, and the testing is repeated, until finally a blue line will be seen at the moment of contact of one drop with the other. If the last negative testing has taken 10.4 cc. from the burette, and this positive testing, which has given the blue line, required 10.6 cc., then the accepted reading would be 10.5 cc., and this would be the hypochlorite equivalent of one-tenth gram of acetone. If the blue line be very faint, it will be momentary only, and will indicate that the excess of hypochlorite is very small, and that 10.6 cc. is a closer reading than 10.5, but the process is not sufficiently accurate to take much account of such differences, since even with much experience and great care it is hardly practicable to get any two titrations to agree within one-tenth cc. of hypochlorite.

Having then 10.5 cc. as the hypochlorite equivalent of one-tenth gram of acetone at this time, it is easy to estimate any smaller or larger quantity of acetone that requires a smaller or larger quantity of the hypochlorite by the equation $10.5 : 0.1 :: a : x$.

But this hypochlorite solution is liable to diminish in strength by keeping, and therefore must be standardized by this standard acetone solution as often as the accuracy of the determinations may require. At times the change in strength is scarcely perceptible from day to day in several successive day's work, but in standing for a week or two there will always be a falling off in strength to the extent of one-tenth to five-tenths cc. in the hypochlorite. The addition of the soda solution appears to render the hypochlorite more permanent, just as the sodium bicarbonate renders the starch solution more permanent. But in the case of the starch the blue reaction does not occur if the bicarbonate be not present.

The titration of the acetone present in unknown dilutions requires first that the strength should be estimated by known conditions or by sensible properties, in order to keep the proportions of the reagents and the dilutions approximately the same, or at least not differing very widely when close determinations are required. If then the taste and smell should indicate that the acetone to be tested is below twenty-five per cent., four-tenths cc. may be taken for the testing. If over twenty-five per cent. and under fifty per cent., two-tenths cc. may be taken. If over fifty per cent., one-tenth cc. is sufficient.

For the adjustment of these small quantities with a sufficient degree of accuracy for rapid technical working, it is convenient to have a five-tenths cc. pipette divided in 0.01 cc. fitted with a rubber bulb, as shown in the illustration. By screwing the neck of this bulb up or down upon the glass, with the point in the liquid, close measurements may be quickly made.

A beaker of fifty cc. capacity containing ten cc. of water is weighed and the weight noted. The four-tenths, two-tenths, or one-tenth cc. of the sample to be titrated is delivered in the water and the weight again taken to give the quantity of the sample taken for the titration. Then the twenty cc. of the iodide and soda solution is added, the whole well stirred, and the hypochlorite dropped in, and the end reaction managed precisely as described in standardizing the hypochlorite, and the quantity of hypochlorite used is noted. Then as 10.5 cc. of the hypochlorite is to one-tenth gram of acetone, so is the quantity of hypochlorite now used to the quantity of acetone present in the portion of the sample taken for titration. Then as the weight of this portion taken for titration is to the quantity of acetone found in it, so is 100 to the percentage of acetone in the sample.

For example, a sample supposed to be not far from absolute is to be titrated. A fifty cc. beaker with ten cc. of water weighs 25.283 grams; with one-tenth cc. of the sample added the weight becomes 25.360 grams, giving 0.077 gram as the weight taken for the titration. To this is added the twenty cc. of iodide and soda solution, and the mixture being well stirred, the hypochlorite is dropped into saturation when seven and nine-tenths cc. is found to have been used. Then as 10.5 is to one-tenth, so is seven and nine-tenths to 0.0752 gram of acetone in the 0.077 gram of the sample taken. Then as 0.077 gram of the sample taken is to the 0.0752 of acetone indicated, so is 100 to 97.66 per cent. of acetone in the sample.

This is the rationale of the operation, but the calculation is shortened by simply dividing the standard hypochlorite (10.5 cc.) into the hypochlorite required (seven and nine-tenths cc.) to get the corresponding acetone (0.0752 gram), and then dividing the weight of the sample taken (0.077 gram) into the weight of acetone obtained from it (0.0752 gram) to get the percentage proportion of the acetone (97.66 per cent.).

Of course the method of definite dilution, and the titration of an aliquot part, as described in the original paper of Robineau and Rollin (see translation) is available and more accurate than that here recommended, and takes but little more time.

Where acetone is made, or is much used, and especially in processes where it is recovered by distillation to be used over again, there is often much need of testing the strength of very weak dilutions, and of knowing when acetone is absent. In many such uses accuracy is not required and rough estimates are sufficient. For work of this kind, especially when the strength is below ten per cent., the weighing of the sample to be tested may be omitted, because the specific gravity is so nearly that of water that the measure may be accepted as cubic centimeter for gram.

DETERMINATION OF ACETONE IN THE PRESENCE OF ETHYL ALCOHOL.

The standard dilution of acetone containing ten grams in the liter was used, and ten cc. of this required 14.3 cc. of the hypochlorite solution. On repetition 14.4 cc. was required.

A dilution of ethyl alcohol was made containing ten grams in the liter, and ten cc. of this requires one-tenth cc. of the hypochlorite. On repetition 0.125 cc. was required.

To ten cc. of the acetone dilution two-tenths cc. of the alcohol dilution was added, and this mixture required 14.4 cc. of the hypochlorite solution. On repetition 14.4 cc. again was required.

To ten cc. of the alcohol dilution two-tenths cc. of the acetone dilution was added, and this mixture required 0.35 cc. of the hypochlorite. On repetition four-tenths cc. was required.

In each case ten cc. of the iodine and soda solution was used and all other conditions were kept fairly uniform.

In the case wherein the hypochlorite was added to alcohol alone no precipitate nor cloudiness was visible, although 0.1 to 0.125 cc. was required to obtain the starch reaction. When acetone had been added to the alcohol one-half this quantity of the hypochlorite was sufficient to give decided cloudiness.

These results appear to confirm the conclusions of Robineau and Rollin to the effect that the presence of ethyl alcohol has no effect upon the titration of acetone by this method, although ethyl alcohol is an iodoform-yielding substance. The small quantity of hypochlorite required to obtain the starch reaction when alcohol alone was titrated was probably in consequence of traces of impurity in the alcohol.

THE DETERMINATION OF SULPHUR IN CAST IRON.

BY FRANCIS C. PHILLIPS.

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IN a paper read before the American Chemical Society in August, 1895,[1] I have detailed some experiments made in the determination of sulphur in white cast iron by the evolution method, and have attempted to show that the loss of sulphur in its

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[1] This Journal, 17, 891.

determination in such iron may be due to the formation of organic sulphur compounds not oxidizable to sulphuric acid by the usual means.

By passing the gases evolved during the solution of the iron in hydrochloric acid through a heated porcelain tube it was found that the volatile organic sulphur compounds may be decomposed and nearly all the sulphur recovered by conversion into hydrogen sulphide, oxidation and precipitation as barium sulphate.

In judging of the correctness of an analytical method it has been necessary in the case of the majority of the constituents of iron to depend upon a single criterion; that method is regarded as most accurate which, being correct in its details, yields the highest percentage of the constituent sought to be determined. For it is hardly possible to add to pure iron a known percentage of sulphur, phosphorus or carbon, and test the method by a determination of the added constituent. For the determination of sulphur in iron it has been common to regard the method of oxidation and solution of the iron by nitric acid, followed by precipitation of the sulphur in form of barium sulphate as the most accurate, inasmuch that it yields results somewhat higher than those obtained by other modes of procedure.

It does not seem probable that an appreciable error could occur in the use of this method unless, in the simultaneous oxidation of the carbon and sulphur of the iron, an organic sulphur compound should be formed.

It has seemed to be of interest, however, to apply a method for the determination of sulphur by which all the constituents of the metal could be completely oxidized in a dry state and at a high temperature, in order to avoid as effectually as possible the chances of loss due to the conversion of sulphur into a volatile compound not oxidizable by ordinary means to sulphuric acid.

In searching for a method which should answer these requirements, it seemed possible that by heating the iron in the form of fine powder in presence of a mixture of alkaline carbonate and nitrate the sulphur might be oxidized directly and completely to the condition of a sulphate without affording an opportunity for the escape of a trace of sulphur in some intermediate volatile or soluble compound. Accordingly an experiment was tried in the following way:

An iron containing its carbon in the combined form was melted in a crucible and poured while fused into water. The granulated metal was crushed in a steel mortar to an extremely fine powder. The powder so obtained was sifted through bolting sheeting.

Two and one-half grams of the sifted iron were mixed with ten grams of a mixture of equal parts of sodium nitrate and carbonate in a platinum crucible. The crucible was covered and heated over a Bunsen burner. At a red heat a sudden and rather violent reaction occurred, and having been begun, was easily maintained with very little aid from the burner flame. The reaction appeared to be complete in a few minutes. After heating for a half hour the crucible was cooled and its contents softened in water. A residue of a reddish brown powder, consisting of ferric oxide with a little ferrous oxide, was obtained. This residue was found to contain no sulphuric acid, and on digesting with hydrochloric acid dissolved without effervescence, showing that none of the particles of the original iron had remained unoxidized. From the results of this experiment and others which need not be detailed here, it seemed to be possible to oxidize finely divided iron so completely by heating with sodium carbonate and nitrate, that its sulphur might be converted quantitatively into sulphuric acid.

The mixture of sodium carbonate and nitrate although tending to oxidize finely divided iron, seems to exert a less powerful action upon the carbon contained in the iron, and this carbon may appear as a black residue after the fused mass has been softened and extracted by water and the ferric oxide dissolved in hydrochloric acid.

It seems to be important for the success of the method that in the oxidation of the iron the carbon should also be nearly or completely oxidized, for if the carbon remained unburned a portion of the sulphur might escape oxidation. In general it may be said that the order of oxidation of these three elements by the method used is as follows: 1, iron; 2, carbon; 3, sulphur; the iron being the most easily oxidized, and the sulphur the most difficult to oxidize. This order is not exactly what we should anticipate, but it is to be remembered that unless the iron grains are fine enough to be penetrated by oxygen, and changed completely into a soft powder of ferric oxide, the sulphur and carbon have no opportunity to oxidize at all. If the iron could be used as an impalpable powder the order of oxidation would probably be different. The marked resistance of the carbon to oxidation has been frequently observed, even when using more sodium nitrate in the fusion than is theoretically enough to completely oxidize both iron and carbon, supposing that the sodium nitrate is reduced only to nitrite in the process.

Experiments of a similar kind were tried with ferromanganese. A metal containing about eighty per cent. of manganese was used. By crushing in a steel mortar this iron was very easily reduced to a powder fine enough to pass through bolting sheeting. On heating the powder with the mixture of sodium nitrate and carbonate a most violent reaction occurred, the metal burning with a long flame, extending several inches above the crucible. In order to control the reaction it was found necessary to melt one-half of the fusion mixture to be used in the crucible and then add slowly the other half, previously mixed with the powdered metal, while stirring constantly. In this way the reaction could be easily controlled. On softening the fused mass in water it was found that the iron had been peroxidized and the manganese changed to binoxide. No trace of sodium manganate was ever formed, the solution in water being after filtration invariably colorless. No carbon was found in the residue. The oxidation of the carbon is much more easily effected in the case of iron containing a high percentage of manganese. In all the trials made the silicon of the iron was oxidized, but it was found that when the fused mass is softened in water very little silica enters into solution as an alkaline silicate, the greater portion remaining insoluble and in a flocculent form.

Experiments were then tried with a gray iron. This form of iron could not be crushed to a fine powder, and an experiment was made in reducing it from small drillings by means of a chilled iron rubber and plate, such as is ordinarily used for grinding ores. Several gray irons were tried in this way. Some could not be powdered by the method just mentioned, the grains tending to flatten instead of being crushed. Others were readily reduced, but the powder was not in any case fine enough for sifting through bolting sheeting. It was found in the case of a gray iron reduced to powder by the method of grinding, that on fusion with the mixture of sodium nitrate and carbonate, used in the preceding experiments, the graphitic carbon of this iron was more readily burnt than the combined carbon of white iron.

As it had proved to be a somewhat difficult matter to oxidize completely the carbon of the iron in the various experiments made with the fusion method, notably in the case of white iron, some trials were made in the use of sodium peroxide. This proved to be a more efficient oxidizing agent for iron and its contained carbon than sodium nitrate. For these trials a mixture was used consisting of forty-five parts each of sodium peroxide and sodium nitrate, together with ten parts of sodium carbonate.

White iron was oxidized and its carbon burnt during a fusion lasting less than ten minutes.

On heating ferromanganese with this mixture the iron was found to be completely oxidized. The carbon was burnt and the manganese was oxidized and converted into sodium manganate, yielding a deep green solution when the fused mass was digested in water.

An admixture of sodium carbonate to sodium peroxide tends in all cases to diminish its action upon finely divided iron at a high temperature and renders the process more easily controlled. It seemed to be possible to base a method for the quantitative determination of sulphur in certain kinds of cast iron upon the reactions described above.

An indispensable condition of success in the use of the method is found in the extreme fineness of the iron. In the case of white irons the fineness of the powder has been secured by crushing in a steel mortar until the powder passed through a sieve of bolting sheeting or bolting cloth.[1]

Some gray irons cannot be crushed or ground. To these the method is not applicable. For gray irons, however, the evolution method answers all requirements.

The following details are given of the method finally employed:

1. *White iron.*—About one and one-half grams of the finely powdered and sifted metal was intimately mixed with eight grams of the sodium peroxide mixture above mentioned, or with four grams each of sodium carbonate and nitrate. The somewhat violent reaction set up on the application of strong heat to the platinum crucible was completed in a few minutes. The crucible was heated for about twenty minutes in all. After cooling the contents were softened in water, the solution decanted and the residue ground, while wet, in a mortar. The solution and residue were then digested in a beaker on the water-bath for one hour after addition of two cc. of strong bromine water. The liquid was then filtered, acidulated with hydrochloric acid, evaporated to dryness to separate the small portion of silica which had entered in solution and filtered. The sulphuric acid was determined in the filtrate in the usual manner. The barium sulphate obtained was always white. If the fusion mixture contains sodium carbonate and nitrate, but no sodium peroxide, the crucible must be heated for a longer time, but a portion of the carbon of the iron may still remain unoxidized.

2. *Ferromanganese.*—In this case it is better to use a mixture of equal parts of sodium nitrate and carbonate, omitting the sodium peroxide.

Ten grams of the mixture were divided into two portions, one of which was fused in a crucible. The other portion mixed with two or two and one-half grams of the finely powdered iron

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[1] Two different materials are sold which are suitable for the sifting. One is called bolting cloth, the other bolting sheeting. The bolting cloth used in these experiments contained about eighty-five meshes to the linear inch, while in the bolting sheeting about one hundred and thirty-five were counted. The material having the smaller number of meshes is made of coarser threads, however, and yields, on account of the smaller openings, a finer powder. Bolting cloth is, on this account, better suited to the preparation of a sample of white iron for a determination of sulphur by the method described.

was then slowly added. Although too violent combustion of the iron is to be avoided, it seems to be important, for the success of the method, that a reaction of decided intensity should occur during the fusion.

Sodium nitrate possesses an advantage over sodium peroxide in its greater purity, the former compound being readily obtainable with practically insignificant traces of sulphur.

Natural gas was the fuel used for the Bunsen burner in heating the charges. This gas was found by repeated experiments, not to contain a sufficient quantity of sulphur to affect the purity of the sodium carbonate when heated in a platinum crucible in the same manner as in the case of the determinations described.

The usual occurrence of sulphur compounds in coal gas would preclude its use in the application of the method.

From the experiments, the results of which are stated in the accompanying table, there seems to be some reason to suppose that not quite all the sulphur of the iron is converted into barium sulphate when the metal is oxidized and dissolved by nitric acid. That it has been completely recovered by the process of fusion cannot be positively asserted.[1]

The method I have described is not proposed as a substitute for any existing method. The purpose of the present work was merely to ascertain as far as possible whether by a process of direct oxidation of the iron in a dry state a larger proportion of the sulphur could be recovered in weighable form than by the usual method of oxidation and solution in nitric acid.

My thanks are especially due to Mr. F. B. Smith for great care and attention to detail in conducting the experiments I have detailed.

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[1] The method of preparation of a sample for analysis in the case of the more brittle forms of iron, by crushing in a steel mortar and sifting, is suggested in Regnault's Elements of Chemistry, translated from the French by Betton, 1867, 2, 112.

Character of iron used.	Fusion mixture employed.	Percentage of sulphur found by fusion.	Percentage of sulphur found by the method of oxidation by nitric acid.
White iron A crushed in mortar and sifted through bolting sheeting.	Contained equal parts of sodium carbonate and nitrate.	0.112	0.101
		0.112	0.098
		0.111	0.096
		0.107	0.099
		0.114	0.100
		0.114	0.102
		0.106	0.102
		0.108	0.104
		0.107	
		0.103	
Means		0.109	0.100
White iron B crushed and sifted.	Contained 45 parts $NaNO_3$ 45 parts Na_2O_2 10 parts Na_2CO_3	0.155	0.143
		0.150	0.149
		0.130	0.143
		0.139	0.147
		0.166	
		0.156	
		0.156	
		0.161	
		0.151	
Means		0.151	0.145
Ferromanganese crushed and sifted.	Contained equal parts of sodium nitrate and carbonate.	0.022	0.012
		0.027	0.013
		0.018	0.012
		0.018	0.010
		0.018	
		0.019	
		0.016	
Means		0.020	0.012
Gray iron drillings powdered by rubber and plate. Not sifted.	Contained equal parts of sodium nitrate and carbonate.	0.034	0.027
		0.030	0.030
		0.036	0.026
		0.034	0.028
		0.033	0.028
		0.034	0.022
Means		0.033	0.027

CARBON DETERMINATIONS IN PIG IRON.

BY BERTRAND S. SUMMERS.

Received October 3, 1896.

THOSE chemists who have had occasion to do many carbon determinations in pig iron, to which was allotted but little time, have probably felt the need of improvements in some of our standard methods.

The old oxygen combustion method, although accurate, requires more time than can usually be spared if use is made of a porcelain or glass tube. However, it has the greatest of all advantages, that of accuracy. The writer has used for some time a regular Bunsen furnace with a glass tube, and while the results were all that could be desired, the time required for a refractory residue was almost three hours.

A series of experiments was conducted with the ordinary chromic acid process, but the results were quite unsatisfactory. Every precaution was taken to insure accuracy, but with high carbon residue low results were obtained in nearly every case when checked by the oxygen combustion method. This was particularly noticeable when a considerable content of graphite was present. The results checked quite well with each other and gave satisfactory results when working on steel.

As this state of affairs greatly embarrassed matters in the laboratory, an effort was made to devise some means by which the carbon could be determined with reasonable speed and accuracy.

Recognizing the advantages of the combustion method, it was decided to make use of a platinum tube. To avoid delay and expense the tube was manufactured in the factory. It was made of 0.200 stock twelve inches long and eleven-sixteenths inch in diameter. A perfectly tight tube was constructed by using ordinary gold solder, which may be obtained from any jeweler. Around each end of the tube copper coolers were brazed, in order to cool the tube in the neighborhood of the rubber stoppers. The inlet of the coolers served the double purpose of supports and water supplies. In spite of this precaution it was found that the air circulating through the heated portion of the tube was hot enough, on reaching the stoppers, to seriously affect them. In order to prevent this, the scheme shown in Fig. 3

was devised. The funnel shape protuberance here seen was filled with ignited asbestos, and the whole was removed with the stoppers. This appliance proved an effectual preventive for further heating of the stoppers, as a red heat could be maintained two inches from them and they remain perfectly cool.

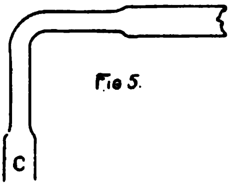


Fig 5.

Fig. 3.

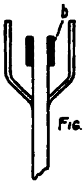


Fig. 4

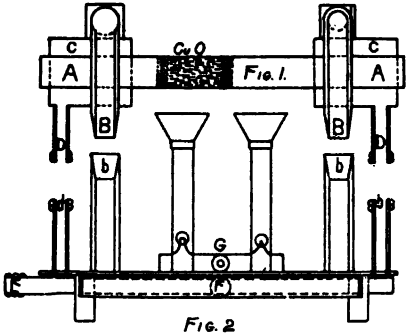
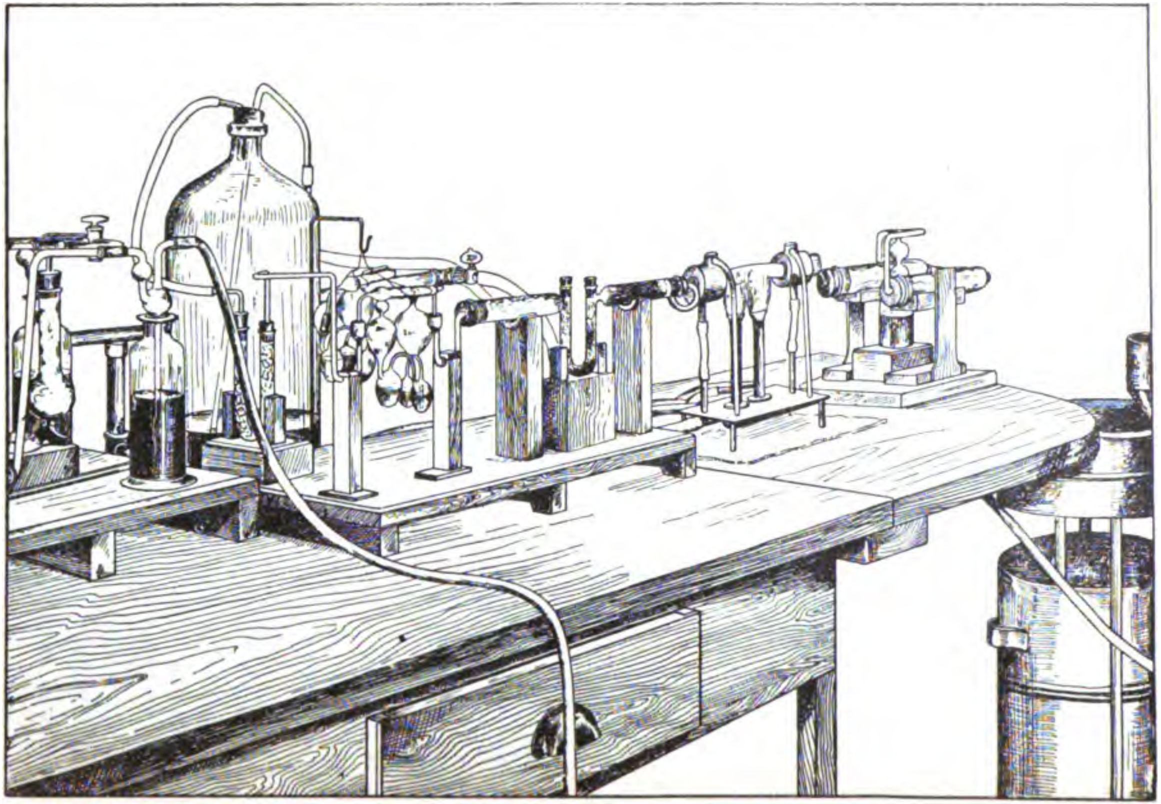


Fig. 2

Fig. 1—*AA*, Platinum tube; *BB*, Support and water outlet; *CC*, Coolers; *DD*, Water supplies.
Fig. 2—*bb*, Sockets for *BB*; *dd*, Connection for water supply, *DD*: *E*, Main water supply; *F*, waste pipe; *G*, Gas connection.
Fig. 3—A_3, Stoppers; A_1, Glass cup for asbestos, A_2; A_4, Outlet.
Figs. 4 and 5—Showing connections for mercury joint.

With this arrangement it was found that a high carbon residue could be burned completely in twenty minutes. It became evident from this that if the aspirating space were decreased, good results could be obtained in a comparatively short time. With this idea in view, the train depicted in the accompanying picture was designed and made by our own glass-blowers. The train has the further advantage that rubber connections are avoided, the only rubber tubing in use being at the ends of the combustion tube.

The purifying train consists of a large U-tube of one and one-half inch stock and twelve inches long. The first limb is filled with broken caustic potash, and the second with fused calcium chloride. The first limb connects with a Drechsel bottle partially filled with strong sulphuric acid, and the second with the combustion tube.



The purifying train on the absorption end is made in one piece. It consists of a five inch U-tube of thick walled glass five-eighths inch in diameter, into the sides of the limbs of which are fused arms. These arms are made of one-inch stock and about seven inches long. The first arm is filled with anhydrous cuprous chloride and anhydrous cupric sulphate. The U-tube serves as the receptacle for the sulphuric acid, and the second arm is filled with calcium chloride previously treated with an excess of carbon dioxide.

The connection with the Geissler bulbs is established by means of mercury joints. These serve to facilitate removal of the bulbs and make a joint which is perfectly secure. The joint can readily be made by any glass blower, an illustration of which is seen in Fig. 4. The end of the Geissler bulb is so reamed as to fit loosely over the tube inside the cup (Fig. 5). A small piece of rubber tubing (*b*, Fig. 4) is slipped over the tube and makes a moderately tight joint with the end of the Geissler bulb. When the cup is filled with mercury a perfect connection is obtained. The method of connecting the Geissler bulb with rubber tubing was both awkward and liable to leakage. These junctions have been in use for some time in our laboratory and have given thorough satisfaction.

With this apparatus as described the most refractory residues are burned in an hour and a half. With residues of less refractory nature and lower carbon content an estimation may be completed in less time. The blank on the apparatus never exceeds three-tenths of a milligram, and is usually one-tenth or nil.

Some results are here appended, thinking they may be of interest. Those obtained by the chromic acid process were quite scattering unless great care was exercised and sufficient time was allowed. The results from this method, given below, are those where much time was given and great pains taken to insure complete oxidation. Values from the Bunsen furnace are given to serve for comparison.

Chromic Acid Method. Total Carbon.	Bunsen Furnace. Total Carbon.
3.23	3.31
3.27	3.33
3.23	...
3.28	...

Results from the above described process, when compared with the Bunsen furnace, were very good.

Platinum Furnace. Total Carbon.	Bunsen Furnace. Total Carbon.
3.03	3.03
3.03	3.05
3.05	...

The convenience of this apparatus in expediting work in the laboratory has led me to write this description, in the hope that it might be of service to other chemists.

CHEMICAL LABORATORY, WESTERN ELECTRIC COMPANY,
CHICAGO.

NOTE ON THE SOLUBILITY OF BISMUTH SULPHIDE IN ALKALINE SULPHIDES.

BY GEORGE C. STONE.

Received November 9, 1896.

IN the August number of this Journal there is a note by Prof. Stillman on this subject; he shows that if a solution containing bismuth is made alkaline by sodium hydroxide and then heated with an excess of an alkaline sulphide a considerable amount of bismuth is held in solution. On repeating his experiments qualitatively I obtained the same result, but when the bismuth was first precipitated as sulphide from an acid solution and then treated with an alkaline sulphide but little if any was dissolved.

To test the solubility quantitatively I made a solution of about one and two-tenths grams of bismuth hydroxide in 500 cc. of very dilute hydrochloric acid; in two portions, of fifty cc. each. I determined the bismuth by precipitation by ammonium carbonate, finding 0.0966 and 0.0965 gram.

I next precipitated the bismuth in two more lots of the same solution by hydrogen sulphide, filtered and heated the precipitate for half an hour with a large excess of potassium sulphide, filtered, dissolved and reprecipitated by ammonium carbonate, the bismuth weighed 0.0981 and 0.0970 gram.

Two more lots treated in the same manner, except that they were heated with ammonium sulphide, gave 0.0970 and 0.0976 gram of bismuth.

From the above it seems fair to conclude that bismuth sulphide precipitated from an acid solution is not dissolved by subsequent treatment with an alkaline sulphide.

[CONTRIBUTION FROM THE LABORATORY OF AGRICULTURAL CHEMISTRY OF THE OHIO STATE UNIVERSITY.]

ON THE BEHAVIOR OF COAL-TAR COLORS TOWARD THE PROCESS OF DIGESTION.

BY H. A. WEBER.

Received October 10, 1896.

IT is very well known that the coal-tar colors have come into general use for coloring confectionery and other articles of food and drink. In fact they have almost completely superseded the vegetable colors, which have been used from time immemorial for a similar purpose. The indiscriminate use of these colors, some of which are derived from bodies of a decidedly poisonous nature, has often been regarded with suspicion by persons who are interested in public health. On account of the uncertainty existing in regard to these colors from a sanitary point of view, Austria has prohibited their use *in toto* in all articles of food and drink. Other countries prohibit certain of the colors, which have been shown to be injurious, and allow all others to be used.

The experiments made upon the lower animals have, in the main, revealed negative results. Thus the writer about eight years ago fed some of the colors most commonly employed by confectioners to rabbits in order to test this question. One-half gram of the colors, among which magenta and corallin were included, was fed to as many rabbits per day for ten days in succession without any apparent ill effects. The exhaustive treatise of Dr. Weil, translated by Leffmann, ascribes toxic effects to only a small number of the many colors employed by him in his experiments upon domestic animals.

The effect which these colors might exert upon digestive ferments, however, was a subject which had as yet received no attention, and the following experiments were undertaken in order to throw some light upon this question. The ferments employed were Armour's pepsin and pancreatine, liberal samples of which were kindly furnished by Armour & Co., of Chicago.

For the purpose of showing the digestive action, blood fibrin preserved in alcohol was employed. The fibrin was soaked and thoroughly washed with water to remove the alcohol, then pressed between filter paper, and the amount required for each experiment weighed off.

In each set of experiments a control experiment was carried on without the addition of color. The mixture was made as follows:

Hydrochloric acid solution (two-tenths per cent.)	100 cc.
Pepsin	20 milligrams.
Fibrin	1 gram.

This mixture placed in a large test-tube was digested in a water-bath at a temperature of 38° to 40° C. until the fibrin was dissolved.

At the same time similar mixtures as above containing in addition 1, 0.5, 0.250, 0.125, and 0.062 gram of the color to be tested respectively, were digested in the same water-bath for the time required to dissolve the fibrin in the control experiment. Any fibrin remaining undissolved in the latter tests, was removed, thoroughly washed, pressed between filter paper as before and weighed.

I. PEPSIN AND OROLINE YELLOW.

This color was one of a series employed in the coloring of confectionery, and was found to be what is known in the trade as *Acid Yellow* or *Fast Yellow*, and is a mixture of sodium amidoazobenzenedisulphonate with sodium amidoazobenzenemonosulphonate.

	Amount of color. Gram	Amount of fibrin. Gram.	Amount of pepsin. Gram.	Duration of experiment. Hours.	Amount of fibrin dissolved. Gram.
1	0.0	1	0.020	3	1.0
2	1.0	1	0.020	3	0.1
3	0.5	1	0.020	3	0.12
4	0.25	1	0.020	3	0.22
5	0.125	1	0.020	3	0.35
6	0.062	1	0.020	3	0.73

From this it will be seen that even in test No. 6, where the color employed amounted to only one part in 1600 parts of the solution, the presence of the color had still a depressing effect. For fear that, owing to the nature of this color, the hydrochloric acid might have been neutralized in part, the experiment was repeated with a six-tenths per cent. solution of hydrochloric acid with similar results.

Of course the determination of the fibrin dissolved is only approximate, as can readily be inferred from the way it was done.

In tests Nos. 2, 3 and 4 no change in the amount of fibrin was apparent to the eye. That a small part of the fibrin had gone into solution was confirmed by the fact that a slight precipitate of albuminoids was obtained on the addition of a solution of tannin. On the whole it must be conceded that this color has a marked and injurious effect upon peptic digestion.

2. PEPSIN AND SAFFOLINE.

This is also a candy color and was found to be *acridine red.*

Amount of color. Gram.	Amount of fibrin. Gram.	Amount of pepsin. Gram.	Duration of experiment. Hours.	Amount of fibrin dissolved. Gram.
0.0	1	0.020	3½	1
1.0	1	0.020	5	1
0.5	1	0.020	5	1
0.25	1	0.020	5	1
0.125	1	0.020	3½	1
0.062	1	0.020	3½	1

As will be seen from the table above, this color only slightly retards the digestion of the fibrin in the three stronger solutions, while in the last two tests there was no interference with the process. On the whole it may be said that the effect of this color on peptic digestion is practically nil.

3. PEPSIN AND MAGENTA.

It is needless to tabulate the results of this experiment. Suffice it to say that the solution of the fibrin in the five tests containing the same proportions of the color as employed above kept pace throughout the whole duration of the experiment with the control test, the fibrin in all cases dissolving at the expiration of three and one-half hours.

This color, therefore, seems not to interfere with peptic digestion.

These four colors were also employed with pancreatin, and the method was as follows:

For the control experiment the following mixture was made :

Water	100 cc.
Sodium bicarbonate	1.5 grams.
Pancreatin	0.3 gram.
Fibrin	1.0 gram.

This mixture contained in a large test-tube, was digested in a water-bath until the fibrin was peptonized. To test the effect of the colors, there was added to similar mixtures as above 1, 0.5, 0.25, 0.125 and 0.062 gram of each color respectively.

5. PANCREATIN AND OROLINE YELLOW.

To the great surprise of the writer, this color, which had proved so effective in stopping and retarding peptic digestion, was found to exert no action whatever on the pancreatic ferment ; the fibrin in all five of the tests with this color, dissolved as freely as that of the control test. The solution of the fibrin in all cases was completed at the expiration of six hours.

PANCREATIN AND SAFFOLINE.

The action of this color was quite different from that of oroline yellow, as the subjoined table will show :

	Amount of color. Gram.	Amount of fibrin. Gram.	Amount of Pancreatin. Gram.	Duration of experiment. Hours.	Amount of fibrin dissolved. Gram.
1	0.0	1	0.3	6½	1.0
2	1.0	1	0.3	6½	0.0
3	0.5	1	0.3	6½	0.0
4	0.25	1	0.3	6½	0.55
5	0.125	1	0.3	6½	0.65
6	0.062	1	0.3	6½	0.75

These results show, that in the two stronger solutions the action of the pancreatic ferment was entirely stopped, and that even in test No. 6, which contained only one part of color to 1600 of the solution the action of the ferment was retarded to a marked extent.

Tannin precipitates the coloring matter.

7. PANCREATINE AND MAGENTA.

This color was as marked in retarding and stopping the action of pancreatine as saffoline. The results are given in the table below :

	Amount of color. Gram.	Amount of fiber. Gram.	Amount of pancreatine. Gram.	Duration of experiment. Hour.	Amount of fiber dissolved. Gram.
1	0.0	1	0.3	6½	1.0
2	1.0	1	0.3	6½	0.0
3	0.5	1	0.3	6½	0.0
4	0.25	1	0.3	6½	0.40
5	0.125	1	0.3	6½	0.60
6	0.062	1	0.3	6½	0.73

The solutions of tests 2 and 3 gave no precipitate with tannin. In all other tests the precipitate was either marked or heavy.

8. PANCREATINE AND METHYL ORANGE.

This color in all of the tests behaved like the last three colors described, completely stopping the action of the pancreatine in the two strongest solutions and retarding it to a marked extent in the weakest. The tabular statement would be similar to the last.

It seems then, so far as these four colors are concerned, that none interfere with both peptic and pancreatic digestion, but that each color interferes seriously with either the one or the other. What the action of other coal tar colors may be, can, of course, not be inferred from this limited number of experiments, but it may safely be said that bodies which have such a decided action in retarding the most important functions of the animal economy, cannot properly have a place in our daily food and drink.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 19.]

THE ACTION OF ACID VAPORS ON METALLIC SULPHIDES.

BY JEROME KELLEY, JR. AND EDGAR F. SMITH.

Received October 2, 1896.

EXPERIMENTS made in this laboratory on the action of the vapors of hydrochloric acid upon the sulphide of arsenic proved that the latter is wholly volatilized. The purpose of the present communication is to record further observations along analogous lines. Thus, when washed and dried arsenic trisulphide is exposed to the action of hydrobromic acid gas, it volatilizes completely. Indeed the action commences in the cold with the formation of a liquid that passes out of the containing vessel upon the application of a very gentle heat. In evidence of this, two quantitative experiments may be given:

Arsenic sulphide taken. Gram.	Arsenic sulphide expelled. Gram.
0.2945	0.2941
0.4632	0.4628

Antimony trisulphide, like that of arsenic, is volatilized by hydrochloric acid gas. It was quite probable that a like deportment would be observed if hydrobromic acid gas should be substituted. This was found to be the case. When the gas came in contact with the sulphide it became liquid and volatilized as soon as a gentle heat was played upon the boat in which the sulphide was contained.

Antimony sulphide taken. Gram.	Antimony sulphide expelled. Gram.
0.1473	0.1469
0.0938	0.0935

Upon substituting stannic sulphide for antimony sulphide, an experience similar to that observed with antimony and arsenic sulphides followed. There was a complete volatilization with but a trifling residue, which proved to be carbon from filter paper that had adhered to the metallic sulphide.

Stannic sulphide taken. Gram.	Stannic sulphide expelled. Gram.
0.1880	0.1880
0.5527	0.5521
0.4174	0.4169

The oxides of arsenic, antimony and tin (at least in the stannic form) can be volatilized in a current of hydrochloric acid gas. This is also true of the sulphides of arsenic and antimony, but how the two sulphides of tin would act under like conditions was not known.

Experiments recently made demonstrate the perfect volatility of stannic sulphide in this way. With stannous sulphide it was found that by the continued action of the gas in the cold there followed a complete conversion into chloride without any volatilization. That the residue was the chloride was evident from its action upon a mercuric salt solution. The figures obtained in the several trials were:

Stannous chloride found. Gram.	Stannous chloride theory. Gram.
0.3544	0.3523
0.4893	0.4903

Several attempts were made to separate stannous and stannic sulphides by this procedure. The results were unsatisfactory. In order to drive out the stannic salt completely it is necessary to heat the mixture, and this caused a partial volatilization of the stannous chloride, so that quantitative results could not be obtained.

Comparatively few metallic sulphides have been studied in the direction indicated in the preceding lines, so that it is probable a wider application of the method will disclose interesting behaviors, and that probably new separations can be brought about in this way. The action of the vapors of haloid acids has also been tried on natural sulphides with a fair degree of success.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 20.]

TUNGSTEN HEXABROMIDE.

BY HERBERT A. SCHAFFER AND EDGAR F. SMITH.

Received October 10, 1896.

THE most recent work upon tungsten bromides is that of Roscoe,[1] who endeavored to prepare a hexabromide, but obtained instead a penta derivative from which the dibromide was subsequently made. By reference to the literature bearing upon this subject it will be noticed that bromine, diluted with carbon dioxide, was made to act upon tungsten metal exposed to a red heat. Experimental evidence is at hand that tungsten at high temperatures deoxidizes carbon dioxide, thus allowing ample opportunity for the production of oxybromides, which, in spite of the greatest care, are sure to appear in larger or smaller amount. The thought also suggested itself that possibly the "red heat" at which the action was allowed to occur might have been detrimental and have indeed prevented the formation of the hexabromide.

Hence, we determined to operate in an atmosphere of nitro-

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[1] *Ann. Chem.* (Liebig), 162, 362.

gen and to apply a very gentle heat to the vessel containing the tungsten. In this connection it may be mentioned that the nitrogen was conducted through a series of vessels charged with chromous acetate, sulphuric acid, caustic potash, and phosphorus pentoxide, respectively. It then entered an empty vessel into which dry bromine was dropped from a tap-funnel, and after passing through a tall tower, filled with calcium chloride, entered a combustion tube resting in a Bunsen furnace. The anterior portion of the combustion tube was contracted at intervals, forming a series of bulbs, and at its extremity was connected with an empty Woulff bottle, followed by a calcium chloride tower, and finally a receiver filled with soda lime and broken glass. A steady current of nitrogen was conducted through this system for a period of three days. On the fourth day bromine was introduced. The tungsten contained in the combustion tube was heated very gently. In a short time brown vapors appeared. These condensed to a liquid beyond the boat and eventually passed into blue-black crystalline masses that separated from the walls of the tube, when perfectly cold, with a crackling sound. Very little heat was required to melt them and they could with care be resublimed in distinct, blue-black needles. The latter was collected in one of the bulbs (No. 2) previously mentioned. Other products were observed and isolated. All were analyzed. Bulb No. 1—that nearest the tungsten metal—contained a black, velvety compound, which upon analysis showed the presence of tungsten dibromide. Bulb No. 2 contained 0.2103 gram of the blue-black crystals, which yielded 0.0577 gram of tungsten, or 27.43 per cent., and 0.1543 gram of bromine, or 73.53 per cent. The theoretical requirements of tungsten hexabromide are 27.72 per cent. tungsten and 72.28 per cent. bromine. The bromine percentage found is high. This may be due to traces of bromine that had not been driven out from the crystalline deposit, or to adherent silver tungstate, as some tungstic acid remained in the solution from which the silver bromide was precipitated.

A fresh portion of the blue-black crystals was prepared as before and analyzed. The bromine determination was unfortunately lost. The determination of the tungsten resulted as follows: 0.4351 gram of material gave 0.1222 gram of tungsten or 28.08 per cent.

A third preparation was made. On subjecting 0.1775 gram of it to analysis these results were obtained:

0.0496 gram tungsten or 27.94 per cent.
0.1266 gram bromine or 71.32 per cent.

Tabulating the series, we have:

		Found.		Mean	Required for hexabromide.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Tungsten......	27.43	28.08	27.94	27.81	27.72
Bromine.......	73.53	71.32	....	72.33	72.28

These figures give evidence that the body analyzed is tungsten hexabromide.

In analyzing the third portion of the blue-black needles the bromine was determined by placing the material in a small Erlenmeyer bulb, covering it with nitric acid and then distilling. The liberated bromine was passed into a silver nitrate solution.

The tungsten hexabromide prepared by us consists, as already observed, of blue-black needles. Moderately elevated temperatures decompose the compound. It gives off fumes when brought in contact with the air. Water decomposes it with the formation of a royal-blue colored oxide. Ammonia water dissolves it, the solution remaining colorless. A vapor density determination resulted negatively, as decomposition was apparent early in the experiment.

NOTES ON THE FERROCYANIDES OF ZINC AND MANGANESE.

BY EDMUND H. MILLER.

Received October 10, 1896.

THE composition of the ferrocyanides of zinc and manganese, formed when salts of these metals are precipitated by potassium ferrocyanide, is given by Prescott and Johnson[1] as $Zn_2Fe(CN)_6$ and $Mn_2Fe(CN)_6$, while the books on volumetric analysis, such as Sutton's and Beringer's, ignore the composition of this precipitate.

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[1] Qualitative Analysis, pages 67 and 57.

The prevailing idea is that in the titration of zinc by potassium ferrocyanide, a normal zinc ferrocyanide is formed. This I believe to be incorrect, for if the reaction is

$$K_4Fe(CN)_6 + 2ZnCl_2 = Zn_2Fe(CN)_6 + 4KCl,$$

a solution of potassium ferrocyanide, one cc. of which is equivalent to ten milligrams of zinc, would contain 32.32 grams of $K_4Fe(CN)_6.3H_2O$ to the liter, not 43.2[1] to 45[2] grams, as has been found by experiment. Using forty-four grams per liter as a basis for calculation, the reaction becomes

$$2K_4Fe(CN)_6 + 3ZnCl_2 = Zn_3K_2(Fe(CN)_6)_2 + 6KCl.$$

This reaction is not merely one that may possibly be true, but according to Wyrouboff,[3] the precipitate formed by the action of potassium ferrocyanide on a zinc salt, whichever is in excess, is $3Zn_2Fe(CN)_6.K_4F_2(CN)_6.12H_2O$, white, while the normal salt, $Zn_2Fe(CN)_6.4H_2O$, is formed only by the action of hydroferrocyanic acid on a zinc salt.

This statement agrees both with the preceding reaction and with the results obtained in standardizing potassium ferrocyanide solution.

The manganese precipitate with potassium ferrocyanide, as obtained in titration, is given by Stone[4] as $Mn_3Fe_2(CN)_{12}$. This is a ferri-, not a ferrocyanide, thus making necessary a change of quantivalence. Mr. Stone also states that an amount of potassium ferrocyanide which will precipitate four atoms of zinc will only precipitate three of manganese, thus basing his calculation on the formation of a normal zinc ferrocyanide.

Wyrouboff[1] gives the precipitate obtained from potassium ferrocyanide and a manganese salt, whichever is in excess, as

$5Mn_2Fe(CN)_6.4K_4Fe(CN)_6.4H_2O$, rose white;

while the normal salt $Mn_2Fe(CN)_6.7H_2O$, cream, is formed as in the case of zinc by hydroferrocyanic acid.

The solution used by Mr. Stone had the following strength:

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[1] Sutton: Volumetric Analysis, p. 329; Beringer: Assaying, p. 219.

[2] Furman: Assaying, p. 205.

[3] *Ann. chim. phys.*, [5], 8. 485.

[4] *J. Am. Chem. Soc.*, 17, 473.

One cc. = 0.00606 gram zinc.
One cc. = 0.00384 gram manganese.

If the ratio were exactly four zinc to three manganese, using the most recent atomic weights, the strength of this solution against manganese would be one cc. = 0.00382 gram, while, according to Wyrouboff, $10Mn = 9K_4Fe(CN)_6$ and $6Zn = 4K_4Fe(CN)_6$, or $10Mn = 13.5 Zn$, or $1Mn = 1.35 Zn$, and the strength against manganese would be 1 cc. = 0.003774 gram.

These figures show but little difference between the two ratios and while Mr. Stone's experimental results are undoubtedly accurate, this theory based on the formation of $Zn_2Fe(CN)_6$ and $Mn_3Fe_2(CN)_{12}$ is not satisfactorily proved.

This article is only a preliminary note regarding the composition of the ferrocyanides as they are being investigated in this laboratory.

In connection with the ferrocyanide of zinc I have found a very strong solution of hydrochloroplatinic acid, H_2PtCl_6, acidified with hydrochloric acid, a most satisfactory indicator for the titration of zinc by potassium ferrocyanide, when performed in a hot solution. This indicator is used in the same way as uranium acetate and is less affected by a varying amount of hydrochloric acid. The end reaction is a bright emerald green, which takes a few seconds to develop. It will not work with a cold solution.

ASSAY LABORATORY, COLUMBIA UNIVERSITY.

A MODIFICATION OF THE GUNNING METHOD FOR NITRATES.

BY JOHN FIELDS.

Received October 20, 1896.

THE full text of the official Gunning[2] method is as follows: "In a digestion flask, holding from 250 to 500 cc., place from seven-tenths to three and five-tenths grams of the substance to be analyzed, according to the amount of nitrogen present. Add thirty to thirty-five cc. of salicylic acid mixture; namely, thirty cc. sulphuric acid to one gram of salicylic acid, shake until thoroughly mixed and allow to stand five to ten

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[1] *Ann. chim. phys.*, [5], 8, 474.

[2] Bulletin 46, U. S. Dept. of Agr., p. 18.

minutes, with frequent shaking; then add five grams sodium thiosulphate and ten grams of potassium sulphate. Heat very gently until frothing ceases, then heat strongly until nearly colorless. Dilute, neutralize, and distil as in the Gunning method."

This method has its advantages in that no heavy metals are added, such as zinc and mercury, which sometimes interfere with the distillation. It has, however, a few disadvantages which the following modification partially overcomes. When working with some materials, there is considerable trouble due to persistent frothing, and in some cases, it has taken six hours constant attention to get the digestion safely over this point. Moreover, unless the contents of the flask are diluted while still warm, there is a tendency for the sulphates to become hard and difficult of solution.

In the modification proposed, the following reagents are necessary:

1. Chemically pure sulphuric acid.
2. Salicylic acid.
3. Potassium sulphide.

The material containing the nitrates is weighed out into a digestion flask and thirty cc. sulphuric acid containing one gram salicylic acid are added, and gently heated to facilitate the solution of nitrates and prevent frothing later. While warm, six to seven grams of potassium sulphide are added in small portions, the flask being thoroughly shaken after each addition. It is then placed over a low flame and the heat rapidly increased until the acid mixture boils. No further attention is required and the digestion is usually complete at the end of an hour. When cold, the liquid is diluted and distilled in the usual manner.

The average difference between the results on sixty samples of fertilizers containing nitrates by the official method and the proposed modification was 0.02 per cent., those by the latter being higher.

The points of difference between the modification and the official modified Gunning are the following:

1. The number of reagents used in the digestion is reduced from four to three.

2. Frothing is obviated and the operation requires no attention except turning up the lamps until full heat is secured.

3. The time of digestion is shortened.

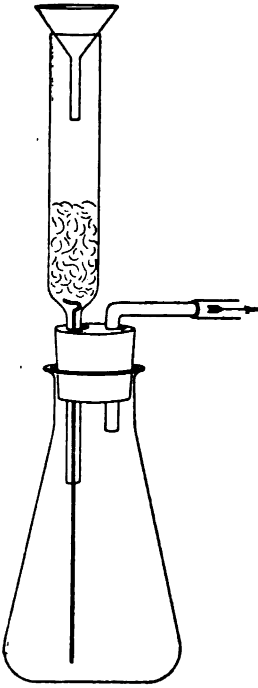
4. Potassium sulphide is made to do double work by acting as a reducing agent instead of sodium thiosulphate and then being converted into potassium hydrogen sulphate serving the end secured by adding potassium sulphate in the original method.

THE SEPARATION OF ALKALOIDAL EXTRACTS.

By Charles Platt.

Received October 20, 1896.

THE writer has found the accompanying simple device of great value in the separation of the annoying emulsions so often met with in alkaloidal analysis, as, for instance, in the petroleum ether and benzene extractions of Dragendorff's method. The filtering tube is nineteen cm. long, the upper 12.5 cm. having an inside diameter of fourteen mm., the lower contracted portion, an inside diameter of three mm. A stout platinum wire bent at the upper end is so placed as to pass through the constricted portion of the tube to the bottom of the eight-ounce Erlenmeyer flask. Washed cotton is firmly packed in the tube to a depth of about four cm. and the apparatus, connected with a filter pump, is ready for use. The filtered liquids may finally be carefully poured into an ordinary separating funnel and manipulated as usual. By this method the most persistent emulsions are separated into their constituent liquids in as many minutes as ordinarily are required hours or days.



Chemical Laboratory, Hahnemann Medical College,
Philadelphia, Pa.

THE PREPARATION OF DIETHYL MALONIC ESTER.

BY W. A. NOYES.

Received October 29, 1896.

HAVING occasion recently to prepare considerable quantities of malonic ester, it has been found that the process can be very much shortened by the use of sulphuric in place of hydrochloric acid and of acid sodium carbonate in place of potassium carbonate. As the body is the starting point for a great variety of syntheses the method used may be of interest to others.

One hundred grams of chloracetic acid are placed in a porcelain dish, 21 cm. in diameter, and 200 cc. of water added. The solution is warmed and ninety grams of acid sodium carbonate added in small portions, and the warming continued until a temperature of 55°–60° is reached and effervescence nearly ceases. Eighty grams of coarsely powdered potassium cyanide is then added, and the whole stirred without further warming, till the somewhat vigorous reaction is complete. The solution is then evaporated rapidly on a thin sheet of asbestos paper till the thermometer with which it is vigorously and constantly stirred shows a temperature of 130°–135°. The hand should be protected by a glove or otherwise, and the glass of the hood in which the evaporation is conducted should be between the dish and the face during this part of the process. The mass should be stirred occasionally while cooling, and as soon as it solidifies it should be broken up coarsely and transferred to a liter flask. Add forty cc. of alcohol and connect with an upright condenser. Through the latter add, in small portions and with frequent shaking, a cooled mixture of 160 cc. of alcohol with 160 cc. of concentrated sulphuric acid. The whole may be added within five or ten minutes (instead of the day and a half required to saturate with hydrochloric acid by the old method). Toward the close there is a considerable evolution of hydrochloric acid. Heat on a water-bath for an hour. Cool quickly under the tap, with shaking to prevent the formation of a solid mass of crystals. Add 200 cc. of water, filter, wash the undissolved salts with about fifty cc. of ether, shake up with the filtrate and separate. Add a solution of sodium carbonate and shake carefully with the ethereal solution till alkaline. Separate again, distil off the ether and dry by heating for fifteen minutes on a water-bath under diminished pressure, using a capillary tube as for vacuum distillations. The residue gives, after one distillation, an almost pure malonic ester.

The sodium carbonate solution appears to contain some of the acid ester. If this solution is added to the first acid solution, the ester separates with some ether. The ethereal solution may be separated, the ether evaporated at a gentle heat, and the residue added to the contents of the flask in which a second saponification of the cyanacetate is to be effected. If this is done, a yield of malonic ester equal to the weight of chloracetic acid used can be obtained. This is ten to fifteen per cent. better than by the old method.

ROSE POLYTECHNIC INSTITUTE,
TERRE HAUTE, IND., Oct. 27, 1896.

NOTE.

Untaxed Alcohol for Use in Manufacturing and in the Arts.—The Joint Select Committee, created at the last session of Congress, to investigate and report upon the question of the use of alcohol free of tax in the manufactures and arts, have prepared a series of interrogatories, which will be distributed throughout the country to such parties as are thought to be interested in the question.

The report of Mr. Henry Dalley, Jr., who was commissioned to investigate the workings of foreign laws governing the use of untaxed alcohol in the manufactures and arts has been submitted, and contains very full and extremely valuable data covering Great Britain, Germany, France, Belgium and Switzerland.

It is the earnest desire of the committee to secure all possible information bearing upon the subject, and it is hoped that parties interested will submit their views to the committee promptly. Sets of the circular letter and blank for replies will be supplied to any applicant by addressing the chairman, Room 21, Senate Annex, Washington, D. C.

The committee, which is composed of three members of each House, will probably assemble in Washington soon after the middle of November for the purpose of formulating a report to Congress accompanied by the draft of a law which will place domestic industries on as favorable a basis as similar industries in foreign countries. During their sessions in Washington hearings will probably be given in order to supplement the information obtained through the interrogatories above set forth. Due notice of the time of such hearings will be given to the public.

OBITUARY NOTICE.

PROFESSOR AUGUST KEKULÉ'S part in the advancement of chemistry has been so important that his death on the 13th of last July has brought a feeling of sorrow to the hearts of chemists throughout the world.

Kekulé was born at Darmstadt, the birthplace of Liebig, on the 7th of September, 1829. It was the intention of his parents that he should become an architect, and he entered the University at Giessen as a student of architecture. He devoted himself with application to the studies bearing on his future calling, but like many another student who came within the range of Liebig's influence, he was filled with an enthusiasm for chemistry, which changed all his plans for the future, and led him to devote himself to this science. It is quite possible that his preliminary architectural studies had much to do with turning his mind toward the ideas of molecular structure or molecular architecture, which he subsequently developed. Kekulé also studied in Paris under Dumas, and in London under Williamson. In 1856 he became privatdocent at the University of Heidelberg. He was appointed professor of chemistry at the University of Ghent (Belgium) in 1858; and in 1865 was called to the University of Bonn, where he remained until his death.

Kekulé's first published work appeared in Liebig's *Annalen* for 1850. Four years later he published his second paper, in which he described thiacetic acid and discussed the action of phosphorus pentasulphide on oxygen acids.

The period from 1854 to 1874 was one of the greatest activity with Kekulé. Since 1874 he has made comparatively few contributions to chemistry, although occasional papers have appeared. In spite of the great number of investigations he has made, chemistry is most indebted to Kekulé for his great generalizations and theoretical suggestions.

He extended Gerhardt's type theory by adding the marsh gas type and introducing the idea of mixed types. These types made clear to him the difference in the power of the elements to hold other atoms in combination, and he developed the idea of valence, first put forward by Frankland, so that this new property of the elements was at once recognized by chemists, the conception of atom-linking followed at once, and this made possible the transition from the type theory to our present conceptions in regard to the structure of compounds.

In this paper published in 1858 Kekulé says: "It is the substitution and relation of the atoms and not radicals, that we must look to in order to get a clearer idea of the nature of these compounds."

He closes this remarkable paper with the following words: "In conclusion I believe that I should emphasize that I do not set much value upon this kind of speculation. But since chemistry, in its entire lack of exact scientific principles, must content itself for the time with the most probable and useful theories; it appears proper to present these views, for they, as it seems to me, give a simple and entirely general expression for the latest discoveries, and because moreover their application may be the means of discovering new facts."

It is not too much to say that the ideas thus modestly put forward, supported by his subsequent work, were the prime cause which led to the abandoning of Gerhardt's types for our present structural formulas.

These ideas had made considerable progress, when in 1865 Kekulé published his now well known hypothesis in regard to the constitution of benzene. Seldom has a theory in chemistry been so suggestive or given rise to so much investigation as this benzene theory. The rich and manifest results accruing from these investigations testify sufficiently to the utility of the theory.

Many students of chemistry were attracted to Bonn; these Kekulé inspired with a love of investigation that has been exceedingly fruitful for the science. Besides his work as a lecturer and investigator, he began in 1860 and finished in 1861 the first volume of his *Lehrbuch der organischen Chemie*, a book that was epoch-making with its new ideas and new methods of presenting this complex subject. The book was received with enthusiasm among chemists, and has served as a model for subsequent works in the same field. Three volumes of this work were finally published, but the work was never completed. He was also for many years one of the editors of Liebig's *Annalen*. During his last years he suffered much from ill health, having followed too literally Liebig's advice: "If you would become a chemist, you must ruin your health. He who does not ruin his health by hard study in these days comes to naught in chemistry."

In 1890 the German Chemical Society celebrated the twenty-fifth anniversary of Kekulé's benzene theory. The meeting was largely attended by chemists from all parts of the world. Addresses were given by A. W. Hofmann, the President of the Society, Adolph von Baeyer, Kekulé's oldest pupil, and by Kekulé himself. A full account of the meeting has been published.[1]

G. M. RICHARDSON.

OCT. 17, 1896.

NEW BOOKS.

MANUAL OF DETERMINATIVE MINERALOGY WITH AN INTRODUCTION ON BLOWPIPE ANALYSIS. By George J. Brush. Revised and Enlarged by Samuel L. Penfield. 14th Edition. pp. ix + 108. John Wiley & Sons. Price, $3.50.

This revision, with the exception of the tables, is practically a new book. The author states that "A complete revision of the tables for the determination of minerals will be made as soon as possible, and a short chapter on crystallography and the physical properties of minerals will be prepared, but until this work can be accomplished, use will be made of the tables and of the short introduction to them from the last edition of Professor Brush."

This proposed revision of von Kobell's table is greatly needed. When it is finished the book bids fair to be as nearly perfect as text-books can well be. The introductory chapter has been rewritten with evident care and by a practiced hand, and as it

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[1] *Ber. d. chem. Ges.*, 23, 1265.

now stands this edition is a great improvement over preceding ones.

"In preparing the introductory chapters, great pains have been taken in the selection of the tests for the elements. Many of them are performed by means of the blowpipe, but chemical tests in the wet way are recommended when it is believed that they are more decisive." To this evidence of good common sense it may be added that in several places the author shows a desire and ability to make his knowledge of practical value. This is shown, for example, under gold, where careful directions are given for the detection of gold in poor gold ores and the like, first by the use of mercury and then without mercury. E. H.

THE ELEMENTS OF CHEMISTRY. By PAUL C. FREER, PH.D. x+284 pp. Boston: ALLYN & BACON. 1895. Introductory price, $1.00.

One feature in particular makes this book especially worth noticing, and that is its outright recognition of the great importance of quantitative work in an elementary course in chemistry. The recognition has been a long time on the way, and its absence has been a great detriment to the chemical instruction in secondary schools.

It is also pleasant to find Professor Freer recognizing that certain so-called physical matters are best reviewed at the outset of such a course. Indeed it would seem as if some such matters which are taken up in the present work, rather late in the course, would better be considered earlier (the laws of Mariotte and Charles for instance).

The book cannot be used to advantage by an inadequately trained teacher, but will certainly be found valuable to the student teacher on account of its excellent collection of experiments which are carefully planned and digested.

JOSEPH TORREY, JR.

TABLES AND DIRECTIONS FOR QUALITATIVE CHEMICAL ANALYSIS. By M. M. PATTISON MUIR.

This little work is evidently intended to increase the possibilities of lecture table instruction in qualitative analysis. It consists of such brief statements of processes and methods as will enable the student to attend to what is going on on the lecture table without running the risk of losing material which ought to get into his note book. The analytical methods described are, for the most part, such as have stood the test of time and experience. JOSEPH TORREY, JR.

THE LIQUEFACTION OF GASES. Papers by MICHAEL FARADAY, F.R.S. (1823–1845). Alembic Club Reprints No. 12. 79 pp. Edinburgh: WM. F. CLAY. Price, two shillings.

In this little book of seventy-nine pages there is much matter that will be of practical service to every one who teaches elementary chemistry. Its value to investigators and advanced students is sufficiently obvious. Students ought to be introduced to the classics of chemistry at a comparatively early stage of their development. They are not as a rule, at present, because the original papers are seldom accessible to the teacher. The publication of Ostwald's "Klassiker" was the first step in the right direction, but the fact that they are in German makes them inaccessible to many who most need them.

JOSEPH TORREY, JR.

CORRESPONDENCE.

POLARIZATION BY DOUBLE DILUTION.

UNITED STATES DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
WASHINGTON, D. C., Nov. 27, 1896.

Editor Journal of the American Chemical Society, Easton, Pa.:

DEAR SIR: By accident a portion of the rule for calculating polarizations by double dilution in our paper published in this Journal, 1896, Vol. 18, pages 428 to 433, was omitted.

Page 430, beginning at the end of line 9, the rule for the approximate calculation of results obtained by Scheibler's method of double dilution should have this addition after the words "small flask," "multiply the difference by two and subtract the product from the reading in the small flask." This is equivalent to multiplying the reading obtained from the solution in the large flask by four and subtracting the reading obtained from the solution in the small flask from the product. The result is the corrected reading and, when a solution of double the normal strength is polarized in a tube of double the normal length, must be divided by four to obtain the percentage. In this case a simpler and equivalent rule for calculation is the following: Subtract one-fourth the reading of the solution in the small flask from the reading in the large flask and the result will be the corrected percentage.

Page 430, end of line 17, the word sucrose should be lactose.

Page 432, the figures in the table in the column headed "Volume of precipitate," were calculated before the exact formula on page 430 was evolved, and are somewhat at variance with the results obtained by use of the formula. The formula gives the following numbers: 5.26, 10.71, 4.88, 9.86, 5.05, 5.41, 4.53, 4.12, 3.87, 4.99, 3.33, 4.22, 16.23. The numbers in the column headed "True volume in 100 cc. flask" must be changed accordingly.

Respectfully,

H. W. WILEY,
E. E. EWELL.

BOOKS RECEIVED.

Bulletin No. 33. Commercial Fertilizers and Chemicals, and Other Information in Regard to Fertilizers. Under the supervision of Hon. R. T. Nesbitt, Commissioner of Agriculture of the State of Georgia. Dr. George F. Payne, State Chemist. Atlanta, Ga.: George W. Harrison, State Printer.

Manual of Determinative Mineralogy, with an Introduction on Blowpipe Analysis. By George J. Brush. Revised and enlarged by Samuel L. Penfield. Fourteenth Edition. x + 108 pp. New York: John Wiley & Sons. Price $3.50.

Jahrbuch der organischen Chemie. Herausgegaben von Gaetano Minunni. Palermo. Zweiter Jahrgang. 992 pp. 1894. Leipzig: Johann Ambrosius Barth. (Arthur Meiner). 1896.

A Brief Introduction to Qualitative Analysis; for Use in Instruction in Chemical Laboratories. By Ludwig Medicus. Translated from the Fourth and Fifth German Editions by John Marshall. Fourth Edition. Philadelphia: Printed by J. B. Lippincott Co. 1896. 203 pp. Price $1.50.

Bulletin No. 43. Second Series. Bovine Tuberculosis in North Louisiana. Bulletin of the Louisiana State Experiment Station, Baton Rouge, La. 1896. 20 pp.

ERRATUM.

On page 994 (November number), seventh line from bottom, instead of "extra internal pressure" read "extra external pressure."

Index to Vol. XVIII, 1896.

References to the pages of the Proceedings are given in Parenthesis.

Issued with January Number, 1896.

Proceedings.

BOARD OF DIRECTORS.

The Board of Directors have passed the following resolutions:

"*Resolved*, That the Board of Directors hereby approve and ratify the action of the majority of said Board, as obtained by their signatures, in granting a charter for a Local Section of the American Chemical Society in North Carolina, and that the charter date from the time said action was taken, November 8, 1895."

"*Resolved*, That the Finance Committee of the American Chemical Society is hereby authorized to approve, and the treasurer to pay to the General Secretary each month during the year 1896 a bill or bills for clerical help, provided, however, that the total sum called for by said bills does not amount to two hundred and fifty dollars ($250.00)."

NEW MEMBERS ELECTED NOVEMBER 21, 1895.

Bailey, Ralph Waldo, Elizabeth, N. J.
Bischoff, Dr. Ernst, 87–89 Park Place, New York City.
Broadhurst, W. Homer, Polytechnic Inst., Brooklyn, N. Y.
Doerflinger, Wm. F., Polytechnic Inst., Brooklyn, N. Y.
Holbrook, Frederick A., 75 Joralemon St., Brooklyn, N. Y.
Jameson, A. H., Cleveland Linseed Oil Co., S. Chicago, Ill.
Le Boutillier, Clement, High Bridge, N. J.
Morgan, J. Livingston Rutgers, New Brunswick, N. J.
Perry, Frank J., B.S., Polytechnic Inst., Brooklyn, N. Y.
Potter, Charles A., 174 Weybosset St., Providence, R. I.
Shaw, Wm. T., Chem. Lab. Agr. Exp. Sta., Bozeman, Mont.
Tucker, S. A., 135 Madison Ave., N. Y. City.
Tyrer, Thomas, Stirling Chem. Works, Stratford, E. England.

ASSOCIATE ELECTED NOVEMBER 21, 1895.

Tuckerman, Alfred, 342 West 57th St., N. Y. City.

NEW MEMBERS ELECTED DECEMBER 13, 1865.

Bellam, Henry Lynch, B.S., Anaconda, Mont.
Cameron, Prof. Frank Kenneth, Catholic Univ. of America, Washington, D. C.

Cushman, Allerton S., Washington Univ., St. Louis, Mo.
Cutts, Henry E., care Stillwell & Gladding, 55 Fulton St., N. Y
Elliott, E. C., care Univ. of Nebraska, Lincoln, Nebr.
Hobbs, Perry L., Western Reserve Medical College, Cleveland, Ohio.
Meisel, C. F. A., 402 Washington St., New York City.
Moore, Chas. C., Jr., Dept. Agr. Div. Chemistry, Washingto D. C.
Schmidt, H. B., 215 E. 4th St., Cincinnati, Ohio.
Stoddard, Dr. H. T., 57 Crescent St., Northampton, Mass.
Thomas, W. S., Belt, Cascade Co., Mont.

ASSOCIATE ELECTED DECEMBER 13, 1895.

Waldman, Louis I., P. O. Box 162, Albany, N. Y.

CHANGES OF ADDRESS.

Appleton, Prof. J. H., 209 Angell St., Providence, R. I.
Benton, Geo. W., 27 E. St. Joe St., Indianapolis, Ind.
Dalton, Parmly, Swampscott, Mass.
Dunham, E. K., 338 E. 26th St., New York City.
Ehrenfeld, A Clemens, Steele High School, Dayton, O.
Feid, George F., 519 Findlay St., Cincinnati, Ohio.
Griffith, Dr. S. H., U. S. Naval Museum of Hygiene, Washington, D. C.
Guiterman, Franklin, care Omaha and Grant Sm. Co., Durango, Colo.
Hewitt, Edward R., 119 E. 18th St., New York City.
Lammers, Theodore L., Helena, Mont.
Textor, Oscar, 158 Superior St., Cleveland, Ohio.
Trubek, M., Raceland, La.
Volckening, Gustave J., 88 Clinton Ave., Brooklyn, N. Y.
Wood, Edward, Harvard Medical School, Boston, Mass.

ADDRESS WANTED.

Grosvenor, Wm., Jr. Last address, Box 166, Johns Hopkins Univ., Baltimore, Md.

MEETINGS OF THE SECTIONS.

NEW YORK SECTION.

The regular meeting was called to order December 6th, 1895. at 8.25, Prof. P. T. Austen in the chair. There were about sixty members present.

The chairman opened the meeting with the statement that Dr. Webb, the President of the College of the City of New York, and Prof. R. Ogden Doremus, had put the chemical lecture room of the college at the disposal of the society; and in his opinion it was the most satisfactory and most favorably situated of any that had yet been considered. He then introduced Prof. Doremus, who said that he was as much surprised as any one at the success of the society's request, as he had been under the impression that there was something in the charter of the college which prevented such use of the room. He remarked that the laboratory was now, since the destruction of the University building, the oldest educational chemical laboratory in the city.

He hoped the society would find it suitable to their purpose and assured it of the heartiest welcome.

The minutes were then read, and the remarks of Prof. McMurtrie in regard to Illinois waters, as reported, were corrected, and the minutes adopted. Prof. McMurtrie moved that the thanks of the Section be sent to President Webb and Dr. Doremus for their courtesy in giving the Section the use of the lecture room. The motion was seconded and carried.

A letter addressed to the chairman from the Secretary of the English Society of Chemical Industry was then read, thanking the New York Section and the Lehigh Valley Section of the American Chemical Society, and the New York Section of the Society of Chemical Industry for the honor done to the President of their Society, Mr. Thos. Tyrer, and the Hon. Foreign Secretary, Mr. Ludwig Mond, on the occasion of their recent visit to New York.

The letter was ordered on file.

Prof. Moale read a paper entitled "A Brief History of Naphthalene," in which the work of the earliest investigators of this interesting substance as well as those in recent years, was reviewed.

Mr. Neiman was called upon by the chairman and gave his experiences in attempting to make naphthalene synthetically, for the purpose of deciding its theoretical constitution.

He stated that the decomposition of certain amido-naphthol-sulpho-acids having a tendency to show that the position of the double bonds in the napthalene ring are not symmetrical, attempts were made to disprove this by the synthetic production of naphthalene from ortho-xylene tetrabromide and ethane. By passing ethane over a heated mixture of granulated pumice stone and ortho-xylene tetrabromide, a portion of naphthalene was formed, but circumstances prevented the further investigation in this line. This formation would seem to show that the central bond is a double one, and the formula a symmetrical one as far as the bonds are concerned.

The second paper of the evening, on "Vegetable Proteids," was read by the author, Dr. T. B. Osborne.

Mr. Hewitt asked if a ten per cent. solution of sodium hydroxide would extract all the proteids or only one, or only a few.

Dr. Osborne replied that all the proteids would dissolve.

Mr. Hewitt had extracted the white bean in large quantities, agitating the bean flour in dilute alkali by machinery, and had obtained a clear solution which filtered readily.

Mr. Hewett asked if there was any difference in the product on repeated precipitations. Dr. Osborne replied, "No, not if they are pure."

Prof. Speyers said that the most interesting point to him was the solubility of the glutinoids in a mixture of alcohol and water, when it appeared that they were insoluble in either water or alcohol alone.

Dr. Osborne thinks there may be a hydrate formed by taking up water from the dilute alcohol, and this hydrate then dissolves.

Dr. Smith said that no one who had not worked in this difficult subject could appreciate the value of Dr. Osborne's work, and especially the classification which had been made of the compounds.

Mr. Hewitt suggested a method of separating the proteids by availing of the different behavior of solutions of different osmotic pressures, and described experiments in which he had used membranes prepared with gelatine treated with formaline, which he found more satisfactory than potassium bichromate or tannin for making the gelatine insoluble. He had also found that the results differed when bichromate or tannin were used.

Prof Austen asked if the vegetable proteids are entirely different from the animal, and if there is any classification of the latter.

Dr. Osborne said that superficially they were. quite similar, but closer study revealed marked differences. Nearly all authors of physiological chemistries give classifications for these proteids, but that most of these authorities differ to a greater or less extent from one another. The most comprehensive classification of the animal proteids that he had seen was that given by Prof. Chittenden in his Cartwright lectures for 1894.

Mr. J. H. Wainwright read a paper on the "Determination of Solid Fats in Artificial Mixtures of Vegetable and Animal Fats." He said that the problem was to make analyses of mixtures of solid fats and vegetable oils, as cottonseed-oil, lard, and oleostearin, which might be classed as compound lards, of which "cottolene" was an example; the chief object being to ascertain the percentage of oleostearin.

In a simple mixture as cottonseed-oil and stearin, the analysis can be readily made by determining the constants of the fat, iodine number, etc. But in a compound lard containing lard itself, the determination of constants gives very little satisfaction, owing to the confusing effect of the lard. Experiments were made on special mixtures with the result of proving that under pressure at ordinary temperatures both cottonseed-oil and lard are removed, leaving the stearin.

At temperatures much above 75° F. or much below 70° F. the error was considerable, but within these limits he had obtained results differing not more than a half per cent. from the correct figure. Until the method was further perfected, he allowed a plus or minus error of one and a half per cent.

CINCINNATI SECTION.

The regular meeting of this section was held on Tuesday evening, December 17, 1895, Dr. Alfred Springer presiding.

Prof. T. H. Norton spoke of the loss sustained by the section in the death of Chauncey R. Stuntz, professor of physics and chemistry at Woodward High School, and moved that Messrs. F. Hornburg, E. Twitchell, S. P. Kramer, and H. B. Foote, all former students of the deceased, be appointed a committee to draft resolutions of respect. Prof. Stuntz was one of the best known educators in the Ohio Valley and one of the organizers of the chemical society of Cincinnati and vicinity, which afterward became the Cincinnati Section of the American Chemical Society. He was elected chairman for 1893; and his earnest work in behalf of the Section was highly appreciated by all the members.

Prof. J. U. Lloyd read a paper on "Percolation" and gave a practical demonstration ot packing the percolator.

The committee appointed to nominate officers for the Section for 1896 reported the following ticket:

President, E. Twitchell.

Vice Presidents, Prof. O. W. Martin and Chas. G. Merrill.

Treasurer, H. B. Foote.

Secretary, E. C. Wallace.

Directors, Dr. S. P. Kramer, Dr. S. Waldbott, Dr. John McCrae,

On motion the secretary was instructed to cast the ballot of the Section in favor of the above ticket.

Issued with February Number, 1896.

Proceedings.

TWELFTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The twelfth general meeting of the American Chemical Society was held in Cleveland, Ohio, December 30th and 31st, 1895.

The first session was called to order by the president, Dr. E. F. Smith, at 9.15 A. M., Monday, December 30th, in the Chemical Lecture Room of the Western Reserve Medical College.

Mr. M. S. Greenough, President of the Cleveland Gas Light and Coke Company, was introduced and gave the following words of welcome:

Gentlemen of the American Chemical Society:

It is with great pleasure that I have accepted the invitation of Prof. Mabery to act as spokesman for the local interests to which you are allied, and welcome you to the hospitalities of our city. Cleveland is a very popular city for conventions, and I am informed that no less than 100 have met here during the year now closing. I venture, however, to assert that no body of men gathered together in this vicinity or elsewhere could represent a profession more useful or honorable than your own. What civilization owes to chemistry is hardly appreciated by the ordinary citizen. He is so accustomed to enjoy the health, comfort and prosperity which comes from it, that he looks upon his blessings as part of the natural order of things, and never stops to consider to what he is indebted for them. When man was in his primitive state and dressed in skins, lived in a tent on what he could kill and changed his residence daily, he naturally had not much use for chemistry, but nowadays without the expert analyst we should be simply helpless. We depend upon him to know that our drinking water is safe to use, whether our children's milk is genuine or diluted, whether our groceries are pure or adulterated. We invoke his assistance in every department of manufacture. In the steel business for instance, which is the right hand of this city, the buyer purchases on a guaranteed percentage of ingredients, and every blow is tested, and where iron ores are saleable or unsaleable according to their chemical composition, there the chemist is absolutely indispensable. It might be truly said that without the constant, persistent, almost unnoticed work of the chemist, this city of Cleveland, with its diversified interests, including every sort of steel work, with its paint works, its refineries, its chemical works and its great ship yards, would be a small town, one-tenth its present size, with gardens and orchards coming down to the Public Square. Cleveland is built on the work of the expert chemist, and yet not one man in a hundred ever stops to realize that fact.

My own business is to furnish illuminating gas to this community and, of course, no man here knows so well as I how much that industry is indebted to chemistry. When I left Harvard College, twenty-seven years ago, and entered the service of the Boston Gas Co., gas sold at $2.50 per thousand; now it is sold there at a dollar, and here this company only nets seventy-five cents for its product, after paying to the city our franchise tax of six and one-half per cent. This is not all due directly to chemistry, but a great part of it is. An old-fashioned gas manager is reported to have said "I don't care a d—n about your hydrogens and your oxygens; you give the coal and I'll cook the gas out of it." Such a man was once very useful, and may be still, but if everybody had held his opinions gas would not now be sold so cheap or pure. There is not a large company in this country to-day but what either employs a permanent chemist or has one near by on whom to call. Before the chemist lent his aid gas companies either ran their tar and ammonia into the nearest river, or else burned their tar and left their ammonia in the gas. Without his experiments and analyses we should never have applied the principles of regenerative gas firing to our retort benches or our gas burners. We should have failed in the successful enrichment of decomposed steam by petroleum products, which has been a development of the last twenty years, and which furnishes the method by which gas can be most cheaply made in many localities in this country.

Auer Von Welsbach was an Austrian chemist who discovered the luminous qualities of some rare earths, by heating which a foot of gas is enabled to give three times as much light as is ordinarily obtained by burning it, and by which gas has been furnished with its strongest weapon in the fight for business. Last of all is this new discovery of calcium carbide with its product of acetylene, which affords the most beautiful artificial light yet produced; and though I am by no means prepared to endorse the claims of its enthusiastic advocates, yet it must have its effect upon the lighting interests of the whole country of every description. "Every man to his last" says the shoemaker, and I speak of these things because they have come under my own eyes; but I have no doubt that every manufacturer in this city might be heard from in a similar strain as to the cheapening and improving of his product by the skill of your profession. I know that I speak for them all when I welcome you to our city, and dwell upon the respect in which we hold you.

You will find upon the programs a large number of enterprises which you are invited to visit. The gas works are not upon the list, but if any of your body are interested in that direction you will find our works on Willson Avenue a good example of modern gas engineering.

I sincerely trust that you will find your stay here both agreeable and interesting, and that we may have the pleasure of seeing you again, either individually or collectively.

If there are any eastern members of your body who are considering the advisability of moving westward, you will, I am sure, take home with you for reflection the great future which is awaiting this city and its environs, and will also realize the opportunities which are awaiting the man who settles among us thoroughly equipped with the education of the industrial chemist.

In response, Dr. E. F. Smith, President of the American Chemical Society, said:

Believe me, sir, that the American Chemical Society fully appreciates the cordial and hearty reception that has been extended to its members, and through me returns to you and those whom you represent, its sincere thanks.

We are glad to be here, and we are eager to avail ourselves of the many opportunities which we shall have while in your midst, of inspecting the many industrial plants within the borders of this city, and within its immediate neighborhood.

We feel particularly grateful to our Council for having called us here, where there is such a centralization of enterprises founded on scientific principles. I can assure you, we will take advantage of the privileges which you have offered to us.

We feel happy, too, in the thought that in coming here we have a chance to meet with your local chemists, who are a host within themselves. They have wrought well, and they have contributed very largely to placing the name of your city upon a high pedestal among the cities of this nation which encourage industries founded upon chemical principles and processes. Two of them particularly are we proud of: I need not mention the names of Dr. Morley and Dr. Mabery, the first of whom has won for himself a reputation by his investigations on certain constants of nature; and the second has achieved equal glory by the researches which he has made, and the light which he has thrown upon the difficulties surrounding the petroleum problem.

For these reasons, and for the opportunities which we hope to have while here of inspecting these great industries, and for the kindly reception given us and the many hospitalities which will be ours while we are here, we thank you.

I trust that you, and all Cleveland for that matter, if convenient, will attend our session and join in the discussions of the papers which are to be presented. (Applause.)

The President then called for the report of the General Secretary, which was read, and by vote of the Society was ordered placed on file. The Secretary's report is as follows:

To the Members of the American Chemical Society:

GENTLEMEN:—The record of the American Chemical Society during the past year has been one of enlarged activities, and of higher attainments and more extended usefulness than ever before. The membership of the Society has steadily increased; three new local sections have been established and many of the older sections have made commendable progress in numbers and in the character and influence of their work; the journal has been much improved, and the Society to-day exerts a more potent influence among chemists, both in the old world and the new, than it did one year ago.

The roll of membership December 26, 1894, was as follows:—Members, 720; associates, 55; honorary members, 8; total, 783. On December 26, 1895, there were 884 members, 58 associates, and 8 honorary members; total 950. If to this number we add the names of 54 persons, who have been elected, but have not yet qualified, (a great majority of them having been elected since the 1st of November, and according to the constitution, not being required to qualify before January 1st), and 31 whose applications for membership are now under consideration, we have a grand total of 1035, which may be considered the present numerical strength of the Society. The increase in membership during 1895 has been greater than in any previous year, except 1894, and there is reason to believe that the momentum which the Society has acquired in this direction during the past few years will continue for a long time to come.

The following named members have died since the presentation of the last annual report of the General Secretary: A. A. Fesquet, H. B. Nason, J. C. Dittrich, W. H. Whalen, Mark Powers, Lewis W. Hoffmann, G. E. Moore, W. G. Wallace and Wm. C. Wilson. This list was reported to the Society at the Springfield meeting last August, and sketches of Prof. Nason, one of the ex-Presidents of the Society, and of Dr. Moore, one of the most highly respected members of the New York Section, have appeared in the Journal of the Society.

The three local sections established during the past year are located respectively in Chicago, Nebraska and North Carolina.

There are now nine local sections of the Society, viz:

Rhode Island Section: Presiding Officer, Charles A. Catlin, 133 Hope St., Providence, R. I.; Secretary, Walter M. Saunders, Olneyville, R. I.

Cincinnati Section: Presiding Officer, Karl Langenbeck, 27 Orchard St., Zanesville, Ohio; Secretary, E. C. Wallace, Room 71, Blymeyer Building, Cincinnati, Ohio.

New York Section: Presiding Officer, Peter T. Austen, Polytechnic Institute, Brooklyn, New York; Secretary, Durand Woodman, 127 Pearl St., New York City.

Washington Section: Presiding Officer, Charles E. Munroe, Columbian University, Washington, D. C.; Secretary, A. C. Peale, 605 12th St., N. W., Washington, D. C.

Lehigh Valley Section: Presiding Officer, Edward Hart, Lafayette College, Easton, Pa.; Secretary, Albert H. Welles, Lafayette College, Easton, Pa.

New Orleans Section: Presiding Officer, A. L. Metz, Tulane Medical College, New Orleans, La.; Secretary, Hubert Edson, Bartels, La.

Chicago Section: Presiding Officer, Frank Julian, South Chicago, Ill.; Secretary, F. B. Dains, 2421 Dearborn St., Chicago, Ill.

Nebraska Section: Presiding Officer, H. H. Nicholson, University of Nebraska, Lincoln, Nebraska; Secretary, John White, Box 675, Lincoln, Nebraska.

North Carolina Section: Officers not yet reported.

The financial outlook of the Society is very encouraging; the report of the Treasurer shows a good balance after paying all indebtedness. A little well directed effort on the part of the members to secure advertisements for the Journal, and increase the regular and associate membership, would add very materially to the income of the Society and would enable the Committee on Papers and Publications to enlarge the scope of the Journal, and to make it in many ways even superior to what it is at present.

The membership dues have been collected by the General Secretary during 1895 as in the previous years. This work has been looked after very closely, and the results have been of twofold advantage to the Society—a considerable sum has been secured that otherwise would have been lost in unpaid arrears, and those who have paid their dues, after repeated reminders from the Secretary, have been saved to the membership of the Society, and have been more prompt the next time in their remittances.

During the year 1895 it has been necessary to drop the names of only twelve persons from the roll of the Society, as required by the constitution, for non-payment of arrears.

During the year Prof. F. W. Clarke resigned as Chairman of the Committee, appointed by the Council, for considering the question of revising the constitution, and Dr. H. W. Wiley was appointed to fill the vacant position. This committee has not yet completed its work. Under the authority and direction of the Society, the General Secretary secured the passage of a bill by the New York Legislature, enabling the Society to choose its directors without regard to their being residents of the State of New York, or any other State or locality, and also legalizing whatever action the Society might take at any of its meetings held outside of New York State.

Prof. Clarke presents his annual report on atomic weights as a paper to be read at this meeting. The Society is to be congratulated in having among its members a person so able and at the same time so willing to present fully a regular annual report upon this subject.

During the year the President, upon the authority of the Council, appointed Messrs. Hale, Austen and Breneman as a committee to consider the question of a permanent badge for the

Society. The committee have met and considered the subject and requests for suggestions and designs have been sent to every member of the Society, but no report has yet been prepared.

The Society held its eleventh general meeting in Springfield, Mass., August 27th and 28th, 1895, just previous to the meeting of the American Association for the Advancement of Science in the same city. There was a large attendance and a full program of papers. The meeting was one of unusual interest and inspiration to all who were fortunate enough to attend. A full account of the proceedings was published in the October number of the Journal.

Early in the year formal invitations were received from the officials of the city of Cleveland, the Chamber of Commerce of Cleveland, the Western Reserve University, the Case School of Applied Science and the Cleveland Chemical Society, for the American Chemical Society to hold their annual meeting this year in Cleveland. These invitations were so hearty, and Cleveland is so desirable a city in which to hold a meeting of the Society, that the Council gladly accepted the invitations, with the result that we are now the favored guests of these bodies and enjoying their cordial and unstinted hospitalities.

It is much to be regretted that every member of the Society could not be present to partake of the rich feast we find prepared for us in this beautiful and enterprising industrial and educational centre.

In looking back upon the past, carefully surveying the present condition and attainments, and anticipating the future, the members of the American Chemical Society have every reason for encouragement and gratification.

If the Society could receive from all its members the loyalty and active support which has always been given by those who have been most devoted to its interests, the rapid progress of the past few years would be regarded as little when compared with what the next decade would witness. May we not hope as we begin this new year in our history that this active support and loyalty will be accorded, and that every member will to the utmost of his ability exert himself to increase the membership, the strength and the influence of the Society, both at home and abroad.

We sometimes feel that we need to establish a league of loyal Americans in the realm of chemical science; whatever Americans accomplish should go to the credit of America. But this is not all; we believe it is a mistake for any chemist under the existing conditions to think that his best path to recognition by the scientific world lies through the medium of foreign periodicals. Articles published in our Journal are so fully abstracted and so often copied entire by foreign scientific periodicals that it seems that the best means for securing general publication and wide spread recognition for any deserving paper is through the columns of our Journal. Thus not only loyalty to the American Chemical Society, but also self interest demands that the columns of our Journal be kept filled with the records of the best work done in our own country.

Respectfully submitted,

ALBERT C. HALE,

BROOKLYN, N. Y., Dec. 26, 1895. *General Secretary.*

FINANCIAL REPORT, 1895.

Received for dues from Dec. 1, 1894 to Dec. 14, 1895	$ 4365.75
Retained as Commission	436.50
Balance for the A. C. S. Treasurer	3929.25
Paid A. C. S. Treasurer (as per vouchers)	3825.00
Balance not yet forwarded	104.25
Interest	11.48
Balance on Deposit	115.73

ALBERT C. HALE,

Dec. 14, 1895. Gen. Sec. A. C. S.

In the absence of the Treasurer his report was read by the General Secretary, as follows:

NEW YORK, December 26, 1895.

TREASURER'S REPORT FOR THE YEAR 1895.

Receipts.

Balance on hand Dec. 21st, 1894	$ 505.95
Net dues and interest received from the Gen'l Secretary	3,940.73
Cash received for subscriptions to Journal	624.93
" " " back numbers	122.82
" " " advertisements in Journal	517.74
Interest from Farmers' Loan and Trust Co	9.80
	$5,721.97

Disbursements.

For expenses of Treasurer's office		$ 11.35
" " " Gen'l Sec'y office		494.03
" " " Editor's office		56.40
" " " Librarian's office		78.18
" " ' Springfield meeting		42.17
" general expenses		67.30
" salary of editor		250.00
" publication of Journal		3,244.15
" insurance		30.00
" rebates to Local Sections, as follows:		
New York Local Section	$ 195.98	
Washington " "	103.33	
Lehigh Valley "	30.00	
Cincinnati " "	60.00	
Chicago " "	38.33	
Nebraska " "	21.67	
		449.13
Balance on hand Dec. 26th, 1895:		
In Farmers Loan and Trust Co	$ 443.63	
In Bank of Metropolis	356.90	
Checks on hand	184.15	
Cash on hand	12.00	
Postage stamps	2.40	
		999.08
		$5,721.97

The following report of the Librarian was read by the General Secretary:

December 26, 1895.

The library has been in storage during the year and therefore there is little to report. It is hoped, however, that a suitable place where the books may be useful to the members will soon be found. Several places have been suggested but none as yet that meets the requirements of the case.

There is a growing call for back numbers of the Journal and I would suggest that the money obtained from their sale be used to find and care for the library.

The Librarian has received the following exchanges:

UNITED STATES.

American Chemical Journal.
American Journal of Pharmacy.
American Manufacturer and Iron World.
American Naturalist.
Annals of the New York Academy of Arts and Sciences.
Anthony's Photographic Bulletin.

Bulletin of the American Museum of Natural History.
Deutsch-Amerikanische Apotheker-Zeitung.
Engineering and Mining Journal.
Ephemeris (Squibb).
Engineering Magazine.
Journal of the Franklin Institute.
Journal of the United States Artillery.
New York Medical Journal.
Oil, Paint, and Drug Reporter.
Popular Science Monthly.
Proceedings of the Academy of Natural Sciences (Philadelphia).
Proceedings of the American Academy of Arts and Sciences (Boston).
Proceedings of the American Philosophical Society (Philadelphia).
School of Mines Quarterly.
Scientific American.
Technology Quarterly.
Textile Colorist.
Textile Manufacturers' Review and Industrial Record.
Transactions of the American Institute of Electrical Engineers.
Transactions of the American Institute of Mining Engineers.
Transactions of the New York Academy of Sciences.

CANADA.

Journal and Proceedings of the Hamilton Association.
Proceedings of the Canadian Institute.
Proceedings and Transactions of the Nova Scotia Institute of Sciences.

HOLLAND.

Revue Internationale des Falsifications.

ITALY.

Gazzetta Chimica Italiana.

ENGLAND.

Analyst.
Chemical News.
Engineering.
Journal of the Chemical Society.
Journal of the Society of Arts.
Journal of the Society of Chemical Industry.
Oil and Colorman's Journal.
Pharmaceutical Journal and Transactions.
Sugar Cane.
Transactions of the Institute of Brewing.

FRANCE.

Annales des Mines.
Bulletin de la Société Chimique de Paris.
Bulletin de la Société Industrielle de Rouen.
Bulletin de la Société Industrielle de Amiens.
Moniteur de la Teniture.
Moniteur Scientifique de Quesneville.
Reportoire de Pharmacie.

GERMANY.

Archiv der Pharmacie.
Bierbrauer.
Bulletin de la Société Industrielle de Mulhouse.
Sitzungsberichte der K. B. Akademie der Wissenschaften zu München.

AUSTRIA.

Allgemeine Oesterreichische Chemiker und Techniker Zeitung.
Oesterreiches Zeitschrift für Berg und Hüttenwesen.
(Proceedings) Kaiserliche Akademie der Wissenschaften in Wien.

RUSSIA.

Bulletin de l'Academie Imperiale des Sciences de St. Petersburg.
Memoirs de la Société des Naturalistes de Kiew.

AUSTRALIA.

Journal and Proceedings of the Royal Society of New South Wales.

ROUMANIA.

Buletinul Societatii de Sciinte Fizice.

The Librarian wishes to acknowledge the receipt of the following volumes:

Chemical Bulletins U. S. Department of Agriculture.
Reports and Bulletins of the Massachusetts Experiment Station.
Reports and Bulletins of the Connecticut Agricultural Experiment Station.
One hundred years of business life, Wm. J. Schieffelin.
An Introduction to the Study of Rocks. Presented by the Trustees of the British Museum of Natural History.

Respectfully submitted,

F. E. Dodge,
Librarian.

Dr. Hart was then called upon and made a report for the Committee on Papers and Publications.

He stated that last year 915 pages of the Journal were published, this year we published 1092 pages, and we have enough papers left over to fill the January number and part of the February number. The committee have been hampered in their plans by the financial condition of the society. But the treasurer's report is an encouraging one, and we hope next year, if we are to go on with the work, to show still better results.

I may say that there are frequent complaints of non-delivery of the Journal from members of the society. The difficulty in most cases is not in the sending out, but with the post office authorities, who are so overwhelmed with second-class matter that they become careless. The Journal is mailed as carefully as it is possible to do it, the address printed and kept standing, and there are very few mistakes made in the office of distribution. I hope that members who do not receive the Journal regularly will write to us, and we will make every effort to get the Journal to them. Very often when a complaint has been made of non-receipt of the Journal, another Journal has been sent, and the second one has not been received. The difficulty seems to be with Uncle Sam's method of conducting business.

Several plans have been suggested and considered for increasing the efficiency of the Journal, but nothing that has been suggested is yet ready for report.

The question of a good journal is largely a financial question. If we have money to print and circulate a journal, we can have a good journal. There is no difficulty about papers. We have more good papers now than we can manage.

It would perhaps be interesting to the members to know something about the actual circulation of the Journal, which is considerably in excess of the membership. We sent out for December 1125 Journals. Of this number less than fifty are exchanges, so our actual paid subscription list is very nearly 1100. The returns for the next year are beginning to come in, and I am able to report large accessions to the number of subscribers, especially foreign subscribers.

Prof. Sabin reported for the Finance Committee.

Formal reports were then made by members of special committees as follows:

Committee on Duty-Free Importation, C. E. Munroe; Committee on Nomenclature and Spelling of the Journal, Edward Hart; Committee on Triennial Congress of Chemists, F. W. Clarke.

The Secretary then read a letter from Dr. T. H. Norton, of Cincinnati, expressing his regret that he was unable to attend the meeting and sending his best wishes for an enjoyable and profitable occasion.

The following communication was then read by the Secretary:

DEPARTMENT OF THE INTERIOR,
UNITED STATES GEOLOGICAL SURVEY.
WASHINGTON, D. C., November 30, 1895.

To the President of the American Chemical Society:

SIR: In compliance with a request emanating from the Chemical Division of this Survey, I address you as the head of the most representative body of American chemists with a view to securing action on the part of the American Chemical Society looking toward the general adoption, in this country at least, of a method for the proximate analysis of coal.

The prevailing method of proximate analysis, though unscientific and far from satisfactory, is still capable of affording information which is valuable, as chemists and geologists know, both as a preliminary to more extended scientific examination and as to the value of coal for one or the other of the uses to which it may be put as a fuel. But in practice such wide diversity exists in the details of this method that the analyses of different series of coals, made by different chemists, are seldom of much value for purposes of comparison, since concordant results are only to be attained by a rigid adherence to a certain order of procedure.

This matter is of great importance to geologists and chemists as well as to those who contemplate investing in coal properties and to many large consumers of coal. A uniform method of analysis, which should also cover the determination of sulphur in coals seems therefore very desirable, and the adoption of such a method can most readily be brought about by the authoritative sanction of the American Chemical Society.

I would make the suggestion that a committee of chemists experienced in coal analysis be appointed with instruction to gather from all sides the views of those whose opinions are likely to be of value in connection with their own, and from the data thus collected to formulate in minute detail a method which may come to be accepted as the one by which all analyses of coal and coke in this country shall be made.

It is not necessary that a novel method be devised, but only that the diversity in detail now practiced be reduced to uniformity by the selection of those features which in the judgment of the committee will most nearly meet the exigencies of the case.

Yours with respect,
CHAS. D. WALCOTT,
Director.

On motion of Prof. Edward Hart it was resolved that the President appoint a committee of three to take into consideration Prof. Walcott's communication and present a report upon the same at the Summer meeting.

After some announcements by the General and Local Secretaries, A. A. Bennett read a paper on "The Quantitative Determination of the Halogens in the presence of each other;" and Wm. McPherson presented a paper on "Constitution of Oxyazobenzene." The latter was discussed by Drs. Prescott, Hart and Mabery.

In the absence of the author a paper by Willis E. Everette on the "Method of Analysis of Nickel and Cobalt in Ores," was read by the General Secretary, and was afterwards discussed by Drs. Mabery and C. B. Dudley.

A. B. Prescott then presented a paper prepared by himself and S. H. Baer on the "Melting Points of Certain Homologous Pyridine Derivatives," and this was followed by another paper entitled "Pyridine Alkyl Hydroxides," by the same authors. These papers were discussed by Drs. Fireman, Smith and Hart. After some announcements the session adjourned.

In the afternoon visits were made to various works in Cleveland, and in the evening the laboratories and lecture rooms of Adelbert College and the Case School of Applied Science were inspected, after which the Society held an evening session.

The evening session of the Society was called to order by President Smith, at 8.15 P. M. in the Chemical Lecture Room of the Case School of Applied Science. After some announcements by the General Secretary, Dr. Chas. F. Mabery was introduced and delivered a very valuable and interesting address upon petroleum. Prof. Mabery gave an account of the experimental methods, products, and results connected with work now in progress on American petroleums. The different forms of stills employed in fractional distillation both under atmospheric pressure and in vacuum were shown, together with the apparatus for distillation under diminished pressure when many operations are in progress. The determination of sulphur in gases, liquids, and solids was described and illustrated by the apparatus.

Representative crude oils from the Oil Springs and Petrolia fields in Canada, from the Lima and Findlay fields in Ohio, and the Berea grit sandstone in Ohio were exhibited and their composition given as well as the composition of representative oil rocks,—the Corniferous limestone, the Trenton limestone, and the Berea Grit sandstone.

A distillation now in operation for the separation of the butanes and pentanes from a very light gasoline (92°) in which a distillate was collecting below —10° was shown in operation, together with other distillates with low boiling points, and their halogen derivatives which are now under examination for the purpose of establishing the identity of the butanes. The purified octanes and some of their halogen derivatives were also described.

Prof. Mabery read a letter from Professor Markownikow of Moscow, which stated that Professor Markownikow had given no attention to Pennsylvania petroleum. In one of his papers, the suggestion had been made that the Pennsylvania oil might prove to contain the naphtenes. This assertion from Professor Markownikow was obtained to correct the erroneous statements in German and American works on petroleum that Markownikow had examined Pennsylvania petroleum.

Professor Mabery exhibited many specimens of hydrocarbons which had been separated from Berea Grit, Ohio, Canada, and Pennsylvania petroleums for the purpose of ascertaining the composition of these oils above 150°.

A number of specimens of sulphur compounds, including sulphides and unsaturated hydrocarbons were shown that had been separated from Canadian petroleum.

After the address several questions were asked of Dr. Mabery and various points were discussed by Drs. Dudley and Prescott; Profs. Moulton and Breneman and Mr. Frasch. Upon motion of Dr. Hale, the Society passed a unanimous vote of thanks to Dr. Mabery. The evening session then adjourned.

The morning session of Tuesday, December 31st, was called to order by President Smith at 9.10 A. M. After some announcements by the General Secretary, the President named the members of the Committee on Coal Analysis, in accordance with the request received by communication from Prof. Walcott. The committee named were: Drs. W. F. Hillebrand, C. B. Dudley, and W. A. Noyes.

Mr. James Otis Handy then read a paper on "Improved Methods for the Analysis of Aluminum, Alumina and Bauxite;" this was followed by a paper on "The Cyanide Method of Extracting Gold from its Ores," by Wm. J. Martin, Jr., read by the General Secretary in the absence of the author.

A paper on "The Use of the Calorimeter in Detecting Adulterations of Butter and Lard," by E. A. de Schweinitz and James A. Emery, was read by Prof. Sabin, the authors of the paper being absent. Prof. Sabin also discussed some of the points contained in this paper.

A paper by H. W. Wiley on "Determination of the Heat of Bromination in Oils," was read by Dr. C. B. Dudley, Dr. Wiley being absent. This paper was discussed by Dr. Dudley and Prof. McPherson.

After some announcements by Dr. Mabery regarding the afternoon excursion, a paper on "Technical Analysis of Asphaltum" by Miss Laura A. Lynton was read by Dr. Prescott, and was discussed by Prof. Sabin, Drs. Mabery and Prescott.

A paper on "The Microscopic Detection of Beef Fat in Lard" by T. S. Gladding, was read by Dr. Hart, after which Prof. F. W. Clarke's Annual Report on the Atomic Weights of the Elements, was read by Prof. Breneman and discussed by Drs. E.F. Smith, Edward Hart, and C. B. Dudley.

The report of the canvassers for the election of officers for the year 1896 was presented by the Secretary and the following named persons were declared elected: President, Chas. B. Dudley; General Secretary, Albert C. Hale; Treasurer, Chas. F. McKenna; Librarian, Frank E. Dodge. Directors to serve two years: Chas. F. Chandler, Peter T. Austen, Chas. E. Munroe, Albert B. Prescott. Councilors to serve three years: J. W. Mallet, Albert B. Prescott, T. H. Norton, G. C. Caldwell.

The retiring President, E. F. Smith, then introduced the President elect, Chas. B. Dudley, with a few congratulatory words to the Society in having secured a man so worthy to occupy the position. After a brief and appropriate response by Dr. Dudley, he was requested to occupy the chair while the retiring President presented his address on "A Glance at the Field of Electro-Chemistry."

On motion of Prof. Sabin, the Society passed a vote of thanks to the Mayor and the Cleveland Chamber of Commerce, the Western Reserve University, Case School of Applied Science and the Cleveland Chemical Society for their kind invitation to hold the Twelfth General Meeting of the American Chemical Society in Cleveland, and for the courtesies extended to the Society during their meeting. The thanks of the Society were also voted to the members of the Local Committee on Arrangements, to the proprietors and managers of the various works visited, to those who received the chemists and conducted them through the works, and to the persons who conducted the various excursions and visits.

Upon motion of Dr. Dudley, a vote of thanks was given to the retiring President, the General Secretary and the Editor for the highly satisfactory manner in which they had discharged the duties of their respectives offices and to those who had prepared papers for the meeting.

Dr. Mabery, President of the Cleveland Chemical Society expressed the great pleasure felt by the people of Cleveland at the honor the Society had conferred upon them in visiting their city, and also the appreciation which they felt of the advantages this visit had conferred upon them.

Dr. A. B. Prescott, one of the Ex-Presidents of the Society was called upon by President Smith for some remarks, and spoke briefly of the rapid growth of the Society, not only in numbers but also in general tone and character of its work. The Twelfth General Meeting of the American Chemical Society was then adjourned.

ALBERT C. HALE,
General Secretary.

EXCURSION TO THE WORKS OF THE GRASSELLI CHEM. CO.[1]

This was the only excursion scheduled for Tuesday afternoon, December 31. It was joined by nearly every visiting and local chemist and was in charge of Mr. Edwin F. Cone, experimental and research chemist of the company. Chemists to the number of seventy-five assembled at a convenient locality and were transported by electric cars to the plant of the company located in the southern part of the city. Here they were met by Messrs. E. R. Grasselli, T. S. Grasselli, J. P. Lihme, gentlemen of the operating department, and others, and were escorted through the plant. This company operates ten different large chemical plants in various parts of the country, one of the largest being the works visited in Cleveland.

The following were the points of interest that were inspected:

Sulphuric Acid.—Several systems are operated here for burning lump and fine ore, the latter being especially adapted for such work. Only pirites is burned obtained from different parts of this country and abroad. The construction of these plants was found to be modern and the equipment equal to the best.

In connection with these systems are the concentrating plants where sulphuric acid in large quantities is concentrated to its various commercial strengths.

Nitric Acid.—In this plant nitric acid was seen in process of manufacture from Chile saltpeter on a large scale. In connection with this was a plant for the production of different grades of acid for the trade.

Hydrochloric Acid.—This plant comprises various modern devices for the manufacture of numerous qualities of muriatic acid. Sodium chloride and nitre-cake are used to a large extent. Salt-cake from these plants is worked up in large quantities and sold to glass manufacturers.

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[1] This description, written by E. F. Cone, was received too late for insertion in the report of the General Secretary.

Mixed Acids.—In this department sulphuric and nitric acids of proper strengths are mixed in such proportions as the trade demands and sold in large quantities to dynamite manufacturers.

Glycerol.—This plant is adapted to the manufacture of chemically pure glycerol, which is obtained on the large scale from crude glycerol by distillation with steam. This department has achieved considerable reputation for the quality of the product, which is equal in every respect to any in the market. Great care is exercised in its manufacture and many chemical tests made to insure a high-grade article. A beautiful product is made and each visitor was presented with a small bottle as a souvenir.

Ammonia.—In this extensive plant large quantities of ammoniacal liquor are worked up into all grades of aqua ammonia, ammonium sulphate and other ammonia products.

Laboratories.—The different laboratories were visited and chemists were found busy in many operations of interest to the analytical and research chemist.

The extensive shops of the company as well as the sal-soda and Glauber's salt plants were also visited.

A pleasant and agreeable surprise awaited the party after the tour of inspection. In the work's office of the company a spread was served, in every way adapted to appease the hunger and quench the thirst caused by the long tour of the afternoon. After the cigars had been passed and a social chat indulged in, the party were transported back to the city by cars. The excursion was voted by one and all a most delightful and instructive one.

BOARD OF DIRECTORS.

Resolved, That the Editor be and he is hereby instructed to mail regularly to the Secretary of each Local Section of the American Chemical Society a copy of the Journal for the use of the section, upon written request of the Chairman and Secretary of the Section.

NEW MEMBERS ELECTED DECEMBER 26, 1895.

Bartlett, Edwin J., Dartmouth College, Hanover, N. H.
Bomberger, F. B., College Park, Md.

Boot, Johannes Cornelius, 24 East 20th St., N. Y. City.
Gray, Marietta, care of University of Nebraska, Lincoln, Neb.
Hilliard, H. J., 204 Columbia Heights, Brooklyn, N. Y.
Hollinger, Myroen John, Sharpsville, Mercer Co., Pa.
Hunicke, H. Aug., 1219 Mississippi Ave., St. Louis, Mo.
Skinner, W. W., College Park, Md.
Summers, Bertrand S., Western Electric Co., Chicago, Ill.
Wigfall, Edward Newton, 1822 Arch St., Phila., Pa.

ASSOCIATES ELECTED DECEMBER 26, 1895.

Allison, William O., William St., N. Y. City.
White, Richard A., Grand Central Station, N. Y. City.

NEW MEMBERS ELECTED JANUARY 18, 1896.

Bartow, Edward, Williamstown, Mass.
Battle, H. B., Ph.D., Raleigh, N. C.
Foulk, Chas. W., B.A., Ohio State Univ., Columbus, Ohio.
Fox, H., 1224 Rookery Building, Chicago, Ill.
Graves, George H., 358 State St., Bridgeport, Conn.
Hall, Clarence, Aetna, Lake Co., Indiana.
Hartwell, Burt L., B.Sc., Kingston, R. I.
Hicks, Edwin F., 52 Beaver St., N. Y. City.
Hopkins, Cyril George, 204 So. 4th St., Champaign, Ill.
Magrunder, E. W., Johns Hopkins Univ., Baltimore, Md.
McGeorge, Arthur, 205 West 78th St., N. Y. City.
Pickering, Oscar W., 2 Milk St., Newburyport, Mass.
Pitman, John R., Frankford Arsenal, Phila., Pa.
Rhodes, Edward, Highfields, Fordsham, Cheshire, Eng.
Sargent, Chas. S., B.Sc., Peace Dale, R. I.
Seal, Alfred Newlin, 1418 Bouvier St., Phila., Pa.
Warwick, Arthur William, Wickes, Mont.
Williams, Charles B., B.S., Raleigh, N. C.
Woodcock, Reginald C., 636 West 55th St., N. Y. City.
Tennille, Geo. F., Ph.D., 519 West 33rd St., N. Y. City.

ASSOCIATES ELECTED JANUARY 18, 1896.

Brenke, Wm. Chas., 506 South 5th St., Champaign, Ill.
Gazzolo, Frank Henry, 930 West Green St., Urbana, Ohio.
Keeler, Harry, 506 South 5th St., Champaign, Ill.

CHANGES OF ADDRESS.

Grosvenor, W. M., Jr., New J. H. Wolfe Hotel, Cripple Creek, Colo.
Guild, F. N., College of Mont., Deer Lodge, Mont.

Johns, John, care of The Guppinheimer Smelting Co., Perth Amboy, N. J.
Jones, L. J. W., 2126 High St., Denver, Colo.
Maury, Geo. P., Braddock, Pa.
Munsell, C. E., 100 Horatio St., N. Y. City.
Parmly, Dalton, 9123 Ontario Ave., Chicago, Ill.
Prochazka, G. A., 138 W. 13th St., N. Y. City.
Rosell, C. A. O., 841 Broadway, N. Y. City.
Townsend, Clinton, U. S. Patent Office, Washington, D. C.
Voorhees, S. S., 2101 G St., N. W., Washington, D. C.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

A meeting was held November 14th, 1895, President Munroe in the chair, with thirty-five members present.

Messrs. H. B. Hodges and Allan Wade Dow were elected as members, and Messrs. W. W. Skinner and F. B. Bomberger as local associates.

Dr. Marcus Benjamin read a paper on "The Smithsonian Institution's Contributions to Chemisry from 1846 to 1896." He recalled the fact that Smithson was regarded as one of the most expert chemists in elegant analysis and thought this fact had much to do with the provision made for a chemical laboratory in the original program of the Smithsonian Institution. He then traced the history of the laboratory of the institution, mentioning the many chemists who have occupied it and whose work has been published by the institution. Among these were J. Lawrence Smith, Dr. Robert Hare, Edward W. Morley, Genth, Gibbs, Booth, Carrington Bolton, Clarke, Traphagen, Magee, and Tuckerman. The paper was concluded with a bibliography of the chemical papers published by the Smithsonian Institution.

Mr. Cabell Whitehead presented "Some Notes of a Recent Visit to European Mints." In the discussion of this paper reference was made to the explosions so common in the lighting of a Buffalo Dental Company's muffle furnace. Mr. Dewey said that these explosions can be avoided by raising the whole body of the furnace by a simple arrangement of movable levers and then slipping a lighted paper over the burner.

Under the title "Calcium Phosphide," Prof. Chas. E Munroe described the process of manufacture which he invented and carried into operation at the U. S. Naval Torpedo Station in 1891. Iron crucibles were employed in which quickline was heated to redness, when white phosphorus in sticks was added through an iron tube which passed through the cover. The process was so simple that it was eventually carried on by unskilled laborers. The phosphide was produced at a cost of twenty cents per pound, while in the market it was selling for $2.25 per pound. It was manufactured for use in automobile torpedoes while at practice, and was found so efficient that when a pound in its container was submerged in eighteen feet of water it gave a flame on the surface two feet in height, which continued to burn intermittently for three hours.

Discussion was by Messrs. Whitehead, Stokes, Kelly and Fireman.

NEW YORK SECTION.

The regular monthly meeting of the New York Section was held at the College of the City of New York, 23d street and Lexington avenue, on Friday evening, January 10th. The usual informal dinner preceded the meeting.

The meeting was called to order at 8:30. Prof. P. T. Austin in the chair; about seventy members present. After the reading of the minutes, Mr. Eimer was asked to describe some improved and novel apparatus which had been placed on exhibition by Messrs. Eimer & Amend.

Mr. G. C. Henning, M.E., delegate for the American Society of Mechanical Engineers to the International Conference at Zurich, 1895, reviewed the "Present Status of Iron and Steel Analysis," calling attention to the discrepancies in some recent work of different chemists in determining the constituents of the same quality of steel, with special reference to carbon and phosphorus, and to the omission of the direct determination of iron, which he thinks conducive to overlooking such elements as titanium, tungsten and others, which are more often present than the usual iron analysis would indicate, as they are but infrequently determined directly.

He reviewed papers by German, French and English authors, giving results of microscopic examination of iron, and methods of preparing the samples for examination, and described the group of carbon "compounds" recognizable under the microscope by suitable methods of surface etching.

He considers that the microscope has opened a field which marks a great advance in methods of determining the condition and quality of iron and steel, and thinks that chemical methods need great improvement to distinguish the conditions in which the carbon exists.

Mr. Rossi in discussing Mr. Henning's paper thought it would be very difficult, if not impossible, to recognize the different combinations of iron and carbon by chemical means, at least in the present state of chemical science, since there is so little outside of physical characteristics to distinguish them.

Prof. Breneman asked whether in a "burned" iron the microscope would show an amount of magnetic oxide proportionate to the degree of deterioration of the iron. Mr. Henning replied that this was practically so; that the oxidation progressed from the surface inward, and a properly polished and etched specimen piece would show, when examined by powers over 800 diameters, the grains of oxide interlaced with the iron, in a form readily distinguishable from the iron.

Dr. McKenna, while admitting the need for chemical methods of determining the number and kind of compounds, is of the opinion that physical methods must be employed in conjunction with chemical methods, and that while chemical methods may advance greatly, the physical methods ought never to be omitted or displaced. Prof. Breneman suggested that the manufacturers would contribute greatly to the advancement of the matter by having the expensive chemical investigations required conducted in their own laboratories at the iron works, where the practical side is already highly developed and the material for research abundantly supplied; and where the results are most wanted and can be instantly applied. He also brought out the looseness of the term "compound" as used by the physicist, and urged the importance of keeping a clear distinction between the true chemical compound and the mixtures which were inaccurately termed compounds. In reply to these remarks, Mr.

Henning said that several steel and iron companies in this country have already established very complete micrographic laboratories, where in three hours an accurate determination of the condition of any specimen of the daily output may be secured.

Mr. George C. Stone read a "Note on the Probable Production of Permanganate by Direct Combustion of Manganese."

In discussing this note, Dr. Rosell called attention to the fact that potassium permanganate, when heated to a red heat, will decompose, and that the other permanganates behave in the same way. In fact, the permanganates can only be made in the wet way. On the other hand, manganates are generally produced in the dry way, and they will stand a very high temperature.

If, therefore, a substance after having been heated to the temperature of the blast furnace, would dissolve in pure water with the well-known rich purple color of a permanganate solution, it seems almost certain that such a substance could not be a permanganate, but it could be a solution of a ferrate.

It is, of course, also possible that the water used for dissolving the substance in question was not pure, but accidentally contained some acid, whereby, on dissolving, the manganate was converted into permanganate.

A second paper by Mr. Stone was entitled "Remarks on Mr. Auchy's Paper on the Volumetric Determination of Manganese." He reviewed the Volhard method and described the conditions under which he obtained the most satisfactory results. He found, that, provided all the iron was oxidized, it made no difference whether nitric, sulphuric, or hydrochloric acid were used. The only difficulty occurred when the amount of manganese was extremely small, in which case it was extremely difficult to get the precipitate to cohere and give a clear solution in which to perceive the end reaction.

Dr. E. R. Squibb presented a paper on the "Manufacture of Acetone and Acetone-Chloroform from Acetic Acid," in which he reviewed the history of acetone from its first mention to the present date. Pelouze was quoted as mentioning acetic acid as the best source of acetone, its vapor being passed through a red-hot tube filled with pumice stone. It was shown that this substance was well known prior to 1848 and had been made in large quantity prior to 1882.

Dr. Squibb described his method of .preparing acetone by destructive distillation of acetic acid, with water vapor in a rotary still.

In regard to acetone-chloroform he quotes Liebig as giving the preference to acetone as the most suitable compound for the preparation of chloroform.

The work of Böttger and Siemerling was described and the results obtained by them were reviewed. One-third of the acetone used was the largest yield of chloroform obtained by Böttger, its specific gravity was 1.31 and it always contained acetone.

The misleading results of Siemerling's work were accepted so implicitly and quoted so definitely in standard works of reference that the further progress of the manufacture of chloroform from acetone was for many years obstructed, and patents have been issued in which the claims were based on supposed improvements on these erroneous results.

The last paper of the evening, " Some Notes on Highly Compressed Gases," was read by Mr. J. S. Stillwell. He described some investigations which had been made of certain explosions of the containing cylinders.

Some investigators had claimed that the passage through a minute orifice of light under high pressure, 2,500 pounds to the square inch, would create sufficient friction and consequent heating to cause explosive union with any oils or fat which might be present, and which might be volatilized by the mentioned source of heat. The author had, in the course of practical experience, tested this point over a hundred thousand times, and was satisfied that the heat never rose to the danger point under normal conditions of working, and that a heat approaching 400° F. was necessary before danger of explosion need be feared. This high temperature of the compressed gas was never reached, except through some careless or accidental want of properly cooling the compressor cylinder.

The meeting adjourned at 11 : 15.

LEHIGH VALLEY SECTION.

The Annual Meeting of the Section was held in the laboratory of Lafayette College, Thursday, Jan. 16, at 3 P. M. The ballots for the election were opened and counted according to the constitution, and the following were found to be elected for the ensuing year:

Presiding Officer: Albert Ladd Colby.
Secretary and Treasurer; Albert H. Welles.
Member of Executive Committee; Edward Hart.

A letter from the General Secretary of the Society of Chemical Industry was read, thanking the Section for their kindness to Thomas Tyrer and Ludwig Mond.

The Secretary was instructed to furnish abstracts of the proceedings, to such journals as might ask for them.

The following papers were presented by Edward Hart: "Note on Some Curious Specimens of Zinc Oxid"; "Note on a Barium Blast Furnace Slag."

He explained that some granulated zinc having been accidently left in an earthenware crucible in a muffle over night, led to the discovery of a most curious formation of zinc oxide, and having designedly repeated the experiments, the results were exhibited.

The barium blast furnace slag was from Nova Scotia. The ore contained 6.30 per cent. barium sulphate, and the slag 3.46 per cent. barium oxide, as the chemist of the company reported it. The question was referred to Prof. Hart how to calculate the barium in the slag, and from the data which he gave he concluded it was neutral, the barium sulphate being reduced to barium sulphide, and existing as such in the slag.

Prof. Richards called attention to the notable amount of aluminum, *viz.*, sixty-three per cent. in the pig iron produced at the furnace mentioned. He cited a case of a furnace in the Juniata Valley, which, under abnormal conditions had produced, as high as one per cent. aluminum, although, as is well known, the presence of metallic aluminum in pig iron is considered inadmissible by some authorities.

Mr. Colby suggested that hereafter a topic be chosen for the evenings discussion, and a leader be appointed to open the discussion and it was decided to adopt the plan at the next meeting.

ALBERT H. WELLES,
Secretary.

NEBRASKA SECTION.

A meeting of the Nebraska Section was held on Thursday, Dec. 19, in the Chemical Laboratory of the University of Nebraska. The meeting was a pronounced success in every way.

The following papers were read: (1) "The Occurrence of Native Iron in Nebraska," by Prof. H. H. Nicholson." (2) "The Effect of Freezing on the Salts in Solution in Spring and Well Waters. Preliminary Notice," by Prof. H. H. Nicholson. (3) "The Description of a Shaking Apparatus for Laboratory Use," by Mr. R. S. Hiltner.

RHODE ISLAND SECTION.

The December meeting of the Rhode Island section was held at Providence on Thursday evening, December 12, 1895, Chairman, Mr. C. A. Catlin presiding.

Mr. J. C. Hebden read a paper upon "The Relation of Acid and Basic Properties of the Artificial Dyes to their Dyeing Properties."

The paper was illustrated with diagrams and dyed samples of wool.

The January meeting was held at Providence, Thursday evening, January 16, 1896, C. A. Catlin in the chair.

A paper upon "Amphoteric Reaction of Milk" was read by W. M. Saunders. After mentioning the results obtained by various investigators upon the subject, the reader described the experiments performed by himself. The milk of about seventy-five cows was examined as to the reaction to litmus paper. The larger number gave a neutral reaction to litmus, the remainder an acid or alkaline reaction in about equal proportion. Cows giving milk with an alkaline reaction to litmus on one day gave the acid reaction a few days later.

CINCINNATI SECTION.

The Section met in regular session Wednesday, January 15, 1896, President Twitchell presiding.

Mr. F. Homburg, chairman of the committee appointed to draft resolutions on the death of Prof. C. R. Stuntz, reported the following:

"Since it has pleased Providence to call from his labors to rest, Prof. C. R. Stuntz, we, the members of the Cincinnati Section of the American Chemical Society, through our committee, desire to express our deep sorrow at the loss of our esteemed friend and colleague, and also our sincere sympathy with all who mourn his death.

"His genial disposition, his courteous bearing, his devotion to science and learning in general, and to the success of our organization in particular, we keenly appreciate.

"The legacy of his noble example will tend to alleviate the distress caused by his departure.

"F. HOMBURG,
"DR. S. P. KRAMER,
"E. TWITCHELL,
"H. B. FOOTE,
"Committee."

On motion of Dr. Springer, the resolutions were adopted, and the committee was instructed to send a copy to the family of the deceased.

Mr. H. B. Schmidt, of Cincinnati, was elected a member of the Section.

Papers were read on "Mercury: Its Occurrence and Production," by Frank I. Shepherd; and "A Few Noteson the Determination of Lead," by J. Hayes-Campbell.

Issued with March Number, 1896.

Proceedings.

COUNCIL.

The following persons have been elected as members of the standing committees for one year:

Committee on Papers and Publications—J. H. Long and Thomas B. Osborne.

Committee on Nominations to Membership—A. A. Breneman, P. T. Austen, and C. A. Doremus.

Finance Committee—Durand Woodman, A. P. Hallock, and A. H. Sabin.

C. F. Mabery has been elected a member of the Council for 1896 in place of Charles B. Dudley, President.

The bills of the Chemical Publishing Co. for $289.24 for the January number and $272.43 for the February number of the Journal, have been approved.

NEW MEMBERS ELECTED FEBRUARY 1, 1896.

Bookman, Samuel, 9 East 62nd St., N. Y. City.
Fullam, Frank L., cor. Gold and John Sts., Brooklyn, N. Y.
Hanks, Abbot A., 718 Montgomery St., San Francisco, Cal.
Lihme, I. P., 27 Tift Ave., Cleveland, O.
Lippincott, Warren B., 3179 Ashland Ave., Chicago, Ill.
Maywald, F. J., 592 Kosciusko St., Brooklyn, N. Y.
Leret, Fred., Virginia, St. Louis Co., Minn.
Sharpless, Fred. F., 811 Wright Block, Minneapolis, Minn.
Stearns, F. C., M.D., 44 Montgomery St., Jersey City, N. J.

ASSOCIATE ELECTED FEBRUARY 1, 1896.

Gordon, Alexander, 44 Montgomery St., Jersey City, N. J.

NEW MEMBERS ELECTED FEBRUARY 24, 1896.

Baker, Theodore, Box 97, Belford, N. J.
Barrett, Jesse M., Purdue University, Lafayette, Ind.
Borland, Chas. R., E. C. Powder Co., Oakland, Bergen Co., N. J.
Cheney, John P., So. Manchester, Conn.
Christiansen, H. B., Hermitage, Floyd Co., Ga.
Jones, Wm. J., Jr., Purdue University, Lafayette, Ind.
Martin, Alex. M., F.C.S., Douglas Villa, Dunbeth, Road, Coatbridge, Scotland.

Myers, H. Ely, Riddlesburg, Bedford Co., Pa.
Slagle, Robert Lincoln, Brookings, S. D.
Smyth, Dr. Geo. A., 900 South Boulevard, Oak Park, Ill.
Tidball, Walton C., care of E. R. Squibb & Sons, Gold and John streets, Brooklyn, N. Y.

ASSOCIATES ELECTED FEBRUARY 24, 1896.

Pomeroy, Thomas W., Lafayette College, Easton, Pa.
Stover, Edward C., Trenton Potteries Co., Trenton, N. J.

CHANGES OF ADDRESS.

Atkinson, Elizabeth A., Three Tons, Pa.
Baekeland, Leo., care Nepera Chem. Co., Nepera Park, N.Y.
Blalock, Thos. L., 3106 O'Donnell St., Baltimore, Md.
Bromwell, Wm., Ph.D., care Tenn. C. I. and R. Co., 1918–1920 Morris Ave., Birmingham, Ala.
Campbell, Geo. F., 80 Bristol St., New Haven, Conn.
Chamberlain, G. D., care N. W. Mall Iron Co., Milwaukee, Wis.
Cornelison, R. W., care McKenzie Bros. & Hill, Bloomfield, N. J.
Doremus, Dr. C. A., 17 Lexington Ave., N. Y. City.
Foote, Henry B., 241 Walnut St., Cleveland, Ohio.
Graves, W. G., 1661 Huron St., Cleveland, Ohio.
Kenan, Wm. R., Jr., care Carbide Mfg. Co., box 45, Niagara Falls, N. Y.
Kiefer, H. E., 16 W. 4th St., South Bethlehem, Pa.
Morse, Fred. W., Lock Box 30, Durham, N. H.
Spencer, G. L., Centralia, Wood Co., Wis.
Trubek, M., 325 Academy St., Newark, N. J.
Walker, Henry V., 38–40 Clinton St., Brooklyn, N. Y.

ADDRESS WANTED.

Johnson, Jesse, last address Augusta, Ga.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The regular monthly meeting of the Washington Section was held December 12, 1895, President Munroe in the chair, with thirty-six members president. In the absence of the Secretary, W. D. Bigelow was elected Secretary, *pro tempore*. The following were elected to membership: W. W. Skinner, F. B. Boneberger, and H. Carrington Bolton. A committee was appointed to arrange for a social meeting of the Section to report at the January meeting.

The first paper of the evening was "Exhibition of Argon and Helium," by Dr. W. F. Hillebrand. He discussed concisely the spectra of argon and helium and closed by exhibiting the spectra to the Society.

The second paper was by Dr. H. W. Wiley, on the "Use of Acetylene Illumination in Polariscope Work, with Illustrations." Dr. Wiley stated that acetylene, while not inferior in point of accuracy to other forms of illumination, is so intense as to permit accurate polarization with solutions so dark in color that they cannot be polarized with lights commonly used for this purpose. He called attention to the "Schmidt and Haensch Triple Field Polariscope," which was said to be a great assistance in both rapid and accurate work. The paper was illustrated with the acetylene light and the polariscope referred to.

Mr. F. P. Dewey read a paper on "The Early History of Electric Heating for Metallurgical Purposes." The paper was comprehensive, embracing the various patents relating to electric heating for metallurgical purposes and also many relating to electric reduction. It was illustrated by photographs and drawings of the various forms of apparatus described.

The last paper of the evening was "A Tribute to the Memory of Josiah P. Cooke," by Dr. Marcus Benjamin. An excellent portrait of Prof. Cooke was exhibited and the sketch of his life was of special interest from the fact that the statements made were from a manuscript sent to Dr. Benjamin some years ago by Prof. Cooke. After discussion by Messrs. Munroe, Tassin, and Wiley, the Section adjourned.

NEW YORK SECTION.

The regular meeting of the New York Section was held at the College of the City of New York on Friday evening, Feb. 7, at 8.30 P. M. The following papers were read: "New Facts about Calycanthus," by Dr. R. G. Eccles, and "Items of Interest from the Cleveland Meeting," by A. A. Breneman.

Dr. Eccles described his work and also that of Dr. H. W. Wiley on the calycanthus seeds and the alkaloids obtained therefrom ; exhibiting the seeds, the principal alkaloid obtained, its salts, the color reactions of both, and the crystalline forms of the salts.

Prof. Breneman described the features of the Cleveland meetmeeting, which were of particular interest to industrial chemists, referring especially to the low pressure distiliation of light petroleum oils as conducted in Prof. Mabery's specially equipped laboratory.

Dr. Durand Woodman exhibited a simple lecture table apparatus for experimentally demonstrating the luminosity of the acetylene flame, generating the gas from calcium carbide.

The meeting was adjourned at 10.45 P. M.

ANNUAL REPORTS OF THE SECTIONS.

The following annual reports from the secretaries of the sections were received by the General Secretary too late for insertion in their proper place:

WASHINGTON SECTION.

Seven meetings have been held and an abstract appended gives the list of papers read and topics discussed at these meetings. The following is a list of the present officers:

President—Charles E. Munroe.

Vice Presidents—E. A. de Schweinitz and W. D. Bigelow.

Treasurer—W. P. Cutter.

Secretary—A. C. Peale.

The officers as above with the following constitute the Executive Committee: H. W. Wiley, F. P. Dewey, F. W. Clarke, and W. H. Seaman. There are no other standing committees.

The secretary of the local section has no way of determining the standing of members. According to a statement made by the General Secretary, December 8, 1894, the membership of the Washington section was sixty-four. As it now appears to be seventy-four the gain during the year is ten.

November 8, 1894.—President W. H. Seaman in the chair. Ten members present. Resignation of Prof. J. C. Gordon read and accepted. Cooperation of the Society asked by John W.

Hoyt in the formation of a "National Post-Graduate University." Prof. H. W. Wiley made a report on the "First Congress of Chemists," at the San Francisco exposition. Paper read by W. D. Biglow on the "Coloring-Matter in California Red Wines."

December 13, 1894.—President W. H. Seaman in the chair Twenty members present. Paper by Oma Carr and J. F. Sanborn on the "Dehydration of Viscous Organic Liquids," read by Mr. Carr. Mr. W. D. Bigelow and E. E. Ewell described a continuous extractor for large quantities of material.

January 10, 1895.—President W. H. Seaman in the chair. Fourteen members present. The following officers were elected: President, Charles E. Munroe; Vice Presidents, E. A. de Schweinitz and W. D. Bigelow; Treasurer, W. P. Cutter; Secretary, A. C. Peale. Additional members of the Executive Committee, H. W. Wiley, F. P. Dewey, F. W. Clarke, and W. H. Seaman. H. C. Sherman, F. P. Veitch, W. G. Brown, and V. K. Chesnut were elected to membership.

February 14, 1895.—The meeting was devoted to the annual address of the retiring president, W. H. Seaman, upon "Chemistry in Education." President Charles E. Munroe in the chair, with members of the Society and invited guests from the Societies of Washington present.

March 14, 1895.—President Charles E. Munroe in the chair. Thirty-five members present. Dr. J. E. Blomén and G. E. Barton elected to membership. The following papers were read: "The Constitution of the Silicates," by F. W. Clarke. "On the Chloronitrites of Phosphorus and the Metaphosphinic Acids," by Dr. H. N. Stokes; "The Manufacture of Soluble Nitrocellulose for Nitrogelatin and Plastic Dynamite," by Dr. J. E. Blomén.

April 11, 1895.—President Charles E. Munroe in the chair. Fifty-three members present. The following papers were read: "The Determination of Nitrogen in Fertilizers," by H. C. Sherman; "Exhibition of Calcium Carbide," by Charles E. Munroe; "Precipitation of Small Quantities of Phosphoric Acid by Ammoniacal Citrate of Magnesia," by E. G. Runyan and H. W. Wiley. The subject for discussion was "Can Argon be Accepted as a New Element?" Discussion was by Charles E. Munroe, F. W. Clarke, T. M. Chatard, and H. N. Stokes.

May 9, 1895.—President Charles E. Munroe in the chair. Forty members present. Messrs. Marion Dorset and S. C. Miller elected to membership. The following papers were read: "A New Meteorite from Forsyth Co., N. C.," by E. A. de Schweinitz; "Hydrogen Fluoride Poisoning," by Peter Fireman; "Progress in the Manufacture of Artificial Musk," by W. H. Seaman. The subject for discussion was "The Chemical Action of Micro-organisms," and was participated in by E. A. de Schweinitz, Surgeon General Sternberg, H. W. Wiley, Prof. George P. Merrill, and R. B. Warder.

The Society adjourned until November.

CINCINNATI SECTION.

The annual election held December 18th, 1894, resulted as follows:

President, Karl Langenbeck; Vice-Presidents, B. D. Westenfelder and I. J. Smith; Treasurer, Henry B. Foote; Secretary, E. C. Wallace; Directors, Dr. S. P. Kramer, Prof. O. W. Martin, H. L. Nickel.

The following were elected chairmen of the standing committees for the year:

1. Didactic Physical and Inorganic Chemistry, Dr. Alfred Springer.
2. Organic Chemistry, Prof. T. H. Norton.
3. Analytical Chemistry, Lewis William Hoffmann.
4. Medical, Physiological and Biological Chemistry, Dr. S. P. Kramer.
5. Technical and Pharmaceutical Chemistry, Prof. J. U. Lloyd.

The following named persons have been elected members of this Section since October 31, 1894: W. G. Wallace, Richard W. Proctor, Charles E. Jackson and George F. Feid, elected December 18, 1894; F. Homburg, E. D. Frohman, elected January 15, 1895; Harry L. Lowenstein, elected February 15, 1895; Prof. A. F. Linn, and Dr. John McCrae, elected October 15, 1895.

In the death of Lewis William Hoffmann and W. G. Wallace the Cincinnati Section sustained a loss of two of its popular younger members, who were highly esteemed by their associates.

Eight meetings were held during the year, at which the following papers were presented. Special meeting held November 7, 1894, addressed by Dr. H. Hensoldt. The subject announced, "Occult Science in the Orient."

Stated meeting December 18, 1894: "Diphtheria Antitoxin," Dr. S. P. Kramer; "Elective Fermentation in Diabetes," Dr. Alfred Springer.

.Stated meeting January 15, 1895: "Separation of the Solid and Liquid Fatty Acids," E. Twitchell; "Report of Progress in Organic Chemistry," Dr. H. E. Newman.

Stated meeting February 15, 1895: Papers announced were postponed on account of sickness of the essayists. "The Difficulty of Obtaining Distilled Water to Meet Pharmacopeial Requirements," was discussed by Prof. Lloyd, Dr. Springer and Prof. Norton.

Stated meeting March 15, 1895: "Determination of Phosphorus in Ferrosilicon," John H. Westenhoff; "The Souring of Milk," Robert W. Hochstetter.

Meeting April 16, 1895: "Recent Important Discoveries in Chemistry," Prof. T. H. Norton.

Meeting May 15, 1895: "Adulteration of Powdered Elm Bark," Henry B. Foote; "Ammonium Thioacetate," Prof. T. H. Norton.

Stated meeting October 15, 1895: "A Tribute to Pasteur," Dr. Alfred Springer; "Laboratory Uses of Aluminum and Recent Progress in Theoretical Chemistry," Prof. T. H. Norton.

A pamphlet issued by the Executive Committee gives names, occupation and addresses of members of the Section, the names of the authors and titles of papers read during 1894.

NEBRASKA SECTION.

The Nebraska Section was organized at a meeting held in Lincoln, June 14, at which meeting officers were selected for the ensuing year, as follows:

President, H. H. Nicholson; Secretary and Treasurer, John

White; Executive Committee, H. H. Nicholson, John White, Rosa Bouton, T. L. Lyon, W. S. Robinson.

The first regular meeting of the Section was held in the Chemical Laboratory of the University of Nebraska on October 30, with a good attendance of members and a number of invited guests.

Papers were read as follows:

By Prof. T. L. Lyon: "The Source of Error in the Estimation of Sugar in Beet Juice by Means of the Sucrose Pipette."

By Mr. Samuel Avery: "Notes on the Electrolytic Determination of Iron, Nickel and Zinc."

Mr. C. H. Suveau, of the Department of Motive Power of the Burlington and Missouri River Railroad, was elected a local associate member.

Other meetings will be held in December, March and June.

Our present membership is thirteen.

CHICAGO SECTION.

The Chicago Section has held but two meetings, one for organization, and the other just reported, at which papers were presented.

The membership is twenty-five.

The officers are as follows:

President, Frank Julian; Vice-President, J. C. Foye; Secretary, F. B. Dains; Treasurer, J. H. Long; Executive Committee, Frank Julian, A. L. Smith, F. B. Dains.

NEW YORK SECTION.

Meetings were held and papers read as follows:

November 9, 1894: "The Rapid and Accurate Analysis of Bone-black," by William D. Horne; "Recent Progress in Physiological Chemistry," by Dr. E. E. Smith.

December 13, 1894: The Chemical Nature of Diastase," by Thomas B. Osborne, of New Haven; "Glucose from a Sanitary Standpoint," by E. H. Bartley, M.D.; "Indiscriminate Taking," by P. T. Austen.

January 10, 1895: "Improvement in the Manufacture of Acetone," by Dr. E. R. Squibb; "Recent Progress in Photographic Chemistry," by Dr. J. H. Stebbins.

February 18, 1895: No quorum.

March 8, 1895: "The Late Prof. Henry B. Nason," by W. P. Mason; "Elective Fermentation in Diabetes," by Alfred Springer; "Note on Absorbent Blocks," by W. H. Broadhurst; "Note on the Precipitation of Iron by Alkali Nitrites," by Gillett Wynkoop; "Volumetric Determination of Zinc and Manganese, and a New Indicator for Ferrocyanides," by G. C. Stone; "Note on the Reduction of Nitrates by Ferrous Hydroxid," by P. T. Austen; "Stability to Light of Haematoxylin Blacks on Wool," by P. T. Austen.

May 11, 1895: "Recent Progress in Analysis of Soils," by H. W. Wiley; "Tribute to the Memory of Dr. Gideon Moore," by C. F. McKenna; "Chemical History of a case of Arsenical and Antimonial Poisoning," by C. A. Doremus; "The Estimation of Acetic Acid in Vinegar," by A. R. Leeds.

June 14, 1895: "Determination of Nitrogen by the Gunning Method," by W. D. Field; "On Asbestos and its Commercial Application," by G. C. Stone; "Examination of Lard for Impurities," by David Wesson; "On Commercial Argol and its Products," by Wm. McMurtrie; "A Modern View of Electro-Chemical Action," by C. L. Speyers; "On the Relation of the Chemical Engineer to Factory Management," by John Enequist.

The informal dinners preceding the meetings have been continued at a majority of the meetings. The total expenditures of the section have amounted to $157.98; those of the preceding year were $160.82. The largest item in each case is the contribution to the Treasury of the Scientific Alliance.

The following officers have been elected for the current year; Chairman, P. T. Austen; Secretary and Treasurer, Durand Woodman; Executive Committee, A. H. Sabin, A. C. Hale, A. R. Leeds; Delegates to Council of Scientific Alliance, P. T. Austen, C. F. McKenna, A. C. Hale.

The list of members is annexed hereto, and shows a total membership of 234 as compared with 183 last year, or a gain of fifty-one members.

RHODE ISLAND SECTION.

The Rhode Island Section of the American Chemical Society respectfully transmits the following general report of the business of the Section for the year September 1, 1894, to September 1, 1895.

The work of the Rhode Island Section for the past year may be described in brief as follows, all the meetings having been held in Providence:

September 27, 1894: A paper prepared by Prof. E. E. Calder upon the "Chemistry of Albuminurea," was read by Mr. W. M. Saunders, the author being unable to be present.

October 18, 1894: A paper was read by Mr. W. M. Saunders upon " Lantern Slides and their Preparation," illustrated by the stereopticon.

December 13, 1894: A paper was read by Charles A. Catlin, upon " Bread and Bread Stuffs."

January 17, 1895: A paper was read by Mr. Geo. F. Andrews upon " The Accuracy of the fire assay of Silver."

February 23, 1895: A paper was read by Prof. J. H. Appleton upon " Argon."

March 21, 1895: A paper was read by Mr. J. P. Farnsworth upon " Selection of water for Bleaching and other manufacturing purposes."

April 24, 1895: A paper was read by Mr. H. C. Burgess upon " A Resumé of the methods of Bleaching Cotton Piece Goods."

May 23, 1895: A paper was read by Mr. E. D. Pearce upon " The coloring-matter of Pollens," with illustrations under the microscope."

June 13, 1895: The Annual Meeting was held at the Hope Club House where the members were entertained at dinner as the guests of the Chairman, Mr. Charles A. Catlin, who presented a paper upon Chemical-Laboratory Microscopy, illustrated by the microscope.

The interest in the local section still continues to be well sustained, and already another new year of its work has begun with very flattering prospects for the future.

At present date the names of the officers of the Section are: Chairman, Charles A. Catlin; Secretary and Treasurer, Walter M. Saunders; Executive Committee, Chairman, ex-officio, Secretary and Treasurer ex-officio, George F. Andrews.

Number of members belonging to the Rhode Island Section at the present time, twenty (20). Net increase over last year two (2).

LEHIGH VALLEY SECTION.

It has been found desirable, as the Section is limited in number, to hold fewer meetings. Four meetings have been held during the past year; *viz.*, November 1, 1894, January 17, May 2, and October 10, 1895. The October meeting was the most successful in the history of the Section, the Society entertaining at that time Thomas Tyrer, Esq., President of the Society of Chemical Industry of England, and invited representatives of the New York Section of the same Society and the New York Section of the American Chemical Society. An inspection of the large government plant of the Bethlehem Iron Co. was made, followed by an elegant dinner tendered the visiting chemists, while the stated meeting was held in the afternoon at Lehigh University.

The following papers have been presented: "Helmholz's Contributions to Science," George P. Scholl; "Castner's Electrolytic Process for Production of Caustic Soda," W. H. Chandler; "A New Ammonia Condenser," Edward Hart; "The Determination of Graphite in Pig Iron," P. W. Shimer; "The Selection of Samples for Analysis," A. L. Colby; "On Standardization of Iodine Solution," G. H. Meeker; "A Device for Sampling Metals," P. W. Shimer; "The Rapid Methods Used in the Bethlehem Iron Co.'s Laboratory," A L. Colby.

Mention should also be made of the interesting paper read by Dr. William McMurtrie at the October meeting, on "Chemical vs. Bacteriological Examination of Water," written by Prof. W. P. Mason.

We close the year with the same number as we began; *viz.*, 21, losses having been made up by new members.

Our annual meeting will be held the third Thursday in January. The officers of the Section for the year 1895 are as follows:

Presiding Officer—Edward Hart.

Treasurer—Albert L. Colby.

Secretary—Albert H. Welles.

Executive Committee—Edward Hart, Albert L. Colby, Albert H. Welles, and J. W. Richards.

THE CLEVELAND EXCURSIONS.

Owing to delay in the receipt of copy it was impossible to give a full account of the meeting at Cleveland in last month's issue. The following additional matter has since been received by the editor:

One very pleasing feature of the meeting in Cleveland was the excursions to various works and other places of interest. Both afternoons were set apart for this purpose, one special party made a trip on Tuesday morning, and on Monday evening the Case School of Applied Science and Adelbert College were visited. Such a large number of excursions were planned, and so many works were freely opened for inspection, that it was impossible to visit them all. Routes Nos. 1, 6, and 7, as given by the local committee's program, were omitted, and all the time available was devoted to the others.

Route No. 2 was led by Mr. D. B. Cleveland, chemist of the American Wire Works.

The first place visited was the plant of the Otis Steel Co. Mr. Bartol, the Superintendent, took charge of the visitors and showed them the plate mill, the basic open hearth furnaces, the steel foundry, the car axle foundry, the machine shop and the laboratory.

The Continental Chemical Co. was next visited. They make red pigments and fuming sulphuric acid from copperas, but had unfortunately been recently burned out, so that it was impossible to see the works.

The manager, Dr. Ramage, exhibited an apparatus for making ozone, which he said brought its cost down to such a point as to warrant its being used for disinfecting garbage, refuse from stock-yards, fats, etc.; for bleaching, for oxidizing sulphurous to sulphuric oxide, thus doing away with the lead chambers in the manufacture of sulphuric acid, and for many other purposes.

He claimed that treatment with ozone is an almost sure cure for consumption in the first two stages and for syphilitic diseases.

He stated that with one-fifth to one-seventh of a horse power he can change one hundred and twenty cubic feet of atmospheric air a minute to a mixture containing fifteen to eighteen per cent. of ozone, all the oxygen present being changed. He uses a fifty volt and two to three ampere alternating current, which he converts to a current of fifty thousands volts.

The Cleveland Nitrous Oxide Co. was next visited, and Mr. Clark and Mr. Hatch showed the party around.

They sell oxygen and hydrogen, epsom salts, liquid nitrous oxide and carbonic acid gas. They also make nitrate of ammonia, as the commercial salt is too impure for their use.

They exhibited some acetylene gas burning from an ordinary gas jet to show the character and illuminating power of this much talked-of new illuminant.

By this time it was too late to visit other places of interest, and the party returned to the hotel.

Route No. 3 was taken on Tuesday morning, the members of this party thus missing the regular morning session. This was done at the suggestion of the Managers of the Varnish works, as their work of boiling varnish could only be seen in the morning. The party was guided by Mr. George Marshall, and included the following places: Cleveland Varnish Co., Cleveland Rubber Co., Glidden Varnish Co., and Warner & Swasey, instrument makers.

A party of six started Tuesday at 9 A.M. from the Hollenden and proceeded to the Cleveland Varnish Co., where Mr. Stark, the chemist, conducted them through the works and explained the different processes. The store-room was first visited, wherein large boxes of rosin are stored, some from New Zealand and some from Zanzibar, the first-named place being the chief source. The gums or rosins used for varnish are amber, fossil and annual; amber and fossil are best, as the thousands of years they have lain in the ground seems to have cured them. These gums are assorted according to color, the lightest being the most valuable. They are found by probing in the sand, in lumps from the size of a bean to that of a wash tub. The largest piece of Kauri gum found weighs 250 pounds. This is the chief gum, but Zanzibar is also used for fine varnishes. These gums are insoluble in common solvents or oil, and must be melted at 560° F. in order to decompose partially, so that they may unite with the oil. The chemists visited the boilers where the operation of dissolving the gum was in progress. These boilers are large vessels, in shape somewhat like the farmer's sap or soap kettles, placed on a small buggy to facilitate removal from the fire. From twenty to twenty-five per cent. is driven off as water and non-drying oils on heating. The latter are unstable, and have not been investigated or utilized, except in connection with the lampblack industry. The gums are prepared for the boilers by hand, as the best size for melting (about that of a hen's egg), is obtained by chopping with a small hatchet. The machines crush them too fine. Linseed oil does not dry quickly unless boiled, and dryers are made by adding a lead or manganese salt to boiled oil. These combine with the oil, forming a compound which absorbs oxygen quickly and hardens. The boilers for oil are the same as for melting, generally larger, with hoods to carry off volatile products. The gum boilers are fitted with covers to decrease loss from spattering and to control the irritating fumes which are carried off by means of tall chimneys. Different solvents, as turpentine, for instance, are used to give required consistency to the finished varnish, and are added to the cooled mixture formed by adding boiled oil to the melted gum. The varnish is then allowed to settle in large tanks for from two months to as many years. The longer the time the finer the varnish made. This is necessary, as filtering does not remove the sediments. The top is siphoned off, filtered through filter presses and run into tanks for ageing. The ageing room is kept at a constant temperature, such that the varnish is fluid, for from nine to eleven months. The party visited the cooper shop, storage tanks, shellac mixers, (which are nothing more than a barrel fastened on a shaft to rotate in the direction of its circumference), and a paint mill of the latest pattern, which does not materially differ from the earliest ones made. The filters were of the well known Johnson's make, and the cloths may be used one day, then removed and agitated in a shellac mixer with turpentine until the gummy sediment is washed out. Each lot of varnish, japan, or enamel after ageing is tried, *i. e.*, some substance for which it will eventually be used as a cover, is coated with it and dried or baked.

The most noticeable feature at the Varnish Co., sets aside the old adage about the shoemaker's wife and blacksmith's colt, for paint and varnish had been used in a very neat and tasty manner throughout the establishment, and what was particularly prominent, was the absolute cleanliness that pervaded even the store-rooms, the settling and ageing rooms, where long lines of tastefully painted tanks pleased the eye, and the excellent arrangement of drafts, hoods, covers and stacks to carry off the offensive odors detrimental to the workman's health.

After visiting the laboratories and drying rooms, the offices were next in order, where a most pleasant surprise was in store. At the invitation of the president, Mr. Tyler, the chemists sat down to a most elaborate luncheon, which was very acceptable. After a vote of thanks had been given their hospitable host, the visitors wended their way to the Cleveland Rubber Co.

Notwithstanding the torn up condition of the rubber company on account of inventory, every courtesy was shown by the foreman of each department, who personally explained his part of the work. The first room visited was the calendering room, where the crude exudings of the South American rubber trees are mangled into workable shape. The rubber gum as received contains fourteen to eighteen per cent. water, and ten to twelve per cent. extraneous matter, such as stones, twigs, bark, etc. Stones are the favorite adulterants, as the crude gum is bought by weight. The gum is first run through rollers upon which water plays, to cleanse it. It comes from the rollers looking like a sheet of thin cork. It is then allowed to cure for three or four months in a dry room at about 70° F. The South American natives cure rubber by exposure to air and sun, so that vulcanization is not necessary, and they make very durable shoes from the product so cured. Modern science has not yet perfected a system for hastening this curing operation, and it is necessary to cure at 70° three or four months since higher heat has a decomposing effect. From the curing room the rubber is passed through slightly heated rollers again and again until it becomes a compact, yielding, non-porous mass. A little vaseline added in this working serves to make the mass more pliable and softens it. From the first rollers it passes to others, where different colored powders are added and worked into the body of the rubber. Pure rubber is black and is useless for many purposes, but by mixing with various constituents it may be impressed into the pores of cloth, making a covering impervious to moisture, rolled into sheets capable of holding gases or liquids, moulded into any shape, hardened by heat, and welded. The fillers, as they are called, are zinc oxide, whiting, lampblack, litharge, sulphide of iron and antimony, and many other substances known only to the trade. Each filler has a different effect on the rubber. Sulphide of antimony is used for fine elastic rubber, such as is used in dental operations and for marine valves. In general, if rubber is to be hardened, as when used for door mats, or if the surface is made impervious to moisture or air for gas bags, water bottles, mackintoshes, hose, bicycle tires, etc., sulphides are used in order that vulcanization may take place after the article is formed. Litharge, lampblack and zinc oxide give color as well as body to the rubber. In order to cover cloth the rubber is wound on rollers and fed through calenders or heated rolls set to such a size that rubber introduced between the rolls in mass is forced through the cloth and becomes part of it; at the same time, by heating the rolls vulcanization also takes place. Vulcanization consists of forming a compound of sulphur and rubber in air by heating, and although it takes much of the elasticity from the rubber, renders it impervious to liquids or gases. Cloth was shown prepared in this way for mackintoshes, hose, etc. Cloth so prepared may be sewed together; a solution of rubber in any volatile solvent applied to the stitches, or the seam covered with a strip of rubber wet with this solution, the whole placed in a steam-heated oven, heated and when withdrawn it is found the cement has welded the holes left by stitches, or the strip upon the original pieces, so that it becomes a compact mass.

The party next visited the molding department. Here the rubber is prepared as above with a filler of some sulphide and then pressed like dough into heated molds. It is very plastic, filling all crevices readily and taking every impression. It does not melt, but the first heat softens it to the consistency of soft taffy, while a greater heat vulcanizes it. In order to keep surfaces in contact from welding together, a little whiting is sprinkled between them. Scraps are reworked, and old rubber, such as boots, is reclaimed and made into coarse articles, such as mats. The mechanical arrangements were (some of them) wonderful, but space cannot be given to a detailed description of them all. As the time for the morning excursion had now been expanded, the party were obliged to forego the pleasure of visiting the other places of interest on the list.

It is to be regretted that more did not avail themselves of the opportunity extended to them to visit these works.

Route No. 4 was for convenience, divided into two excursions, the Grasselli Chemical Works being visited on Tuesday and the other places on Monday.

The trip to the Oil works was under the guidance of Mr. H. L. Payne, chemical engineer, and the visitors were introduced to the practical side of a subject, whose chemical side was so interestingly presented by Dr. Mabery in his address on the same evening. Only one refinery was visited.

The one selected is not under the control of the Standard Oil Co., and works up all of its own product. The visitors were therefore fortunate in being able to see within the confines of one muddy hillside all the branches of this vast industry. The members of this firm, Messrs. Scofield, Shurmer & Teagel, were all very obliging, and Mr. Daniel Shurmer and his son personally conducted the party through the extensive works.

The stills are sheet steel tanks set in brick work and have an open coal fire under them. Some are set on end and others lie on the side. They are not usually covered in like a boiler, but exposed to the air on top and sides, and only protected from the weather by a rough shed. This circumstance would seem to cause a waste of fuel, but it probably assists in the proper "cracking" of the oil. The distillate is condensed in a series of wrought iron pipes, which are kept cool by immersion in a long wooden trough. The trough is kept filled with cold water from springs in the side hills. Various methods of procedure are adopted in the distillation, depending upon the character of the product desired, for not all of the various oil products are or can be made in one distillation. The lighter and more volatile products are usually collected together and then redistilled with steam heat in order to separate them into commercial "naphtha," "benzine," "gasoline," etc. In this distillation the steam is introduced directly into the oil and the condensed water is drawn off at the bottom of the still-tank. The very light vapors and gases which come off first are sucked down by a steam syphon and burned under the boilers.

The residue left in the crude oil stills may be either a thick tarry pitch or the distillation can be carried so far that only a porous coke is left. This coke contains only 0.01 to 0.02 per cent. ash, and is in great demand for the manufacture of electric light carbons.

The burning oils are all purified by washing in a huge lead-lined separatory funnel, called an agitator. They are first washed with concentrated sulphuric acid which unites with and precipitates the basic matters, such as phenol. The oil after this washing contains less oxygen than before. The principal object of this treatment is to remove those bodies which would cause a coloration of the oil; a water-white kerosene is supposed to best suit the consumer. The excess of acid is washed out with water or steam and the oil is completely neutralized by a little caustic soda. This refinery is using some Lima oil, and they treat it with litharge in the agitator to remove the sulphur. Other refineries use copper oxide in their stills for the same purpose.

One of the most interesting products of crude oil is paraffin. It distills over as a greenish oil, and the visitors were permitted to examine the crystallizing process where the solid wax is frozen out and filtered from the more liquid part of the oil. A second or third treatment of the crude wax with solvent naphtha and this freezing process, turns out the pure white chewing gum. Every paraffin works has its own ammonia freezing plant.

Most of the refineries have no chemist in their employ. They are mainly concerned with the physical properties of their products, and a boy soon learns to make the test for specific gravity, flashing point, burning point, freezing point and viscosity.

The cooperage and shipping departments were large and interesting, but when the party arrived at that portion of the works they were ready to return to the hotel.

The other excursion of Route No. 4 was taken by all on Tuesday morning. The Grasselli Company's works are of such magnitude that a description is impossible. They make sulphuric acid, nitric acid, hydrochloric acid, mixed acid for nitroglycerol factories, ammonia, glycerol, and all the various salts and bye products of such an industry. Mr. E. F. Cone, chief chemist of the experimental laboratory, was the conductor on this occasion, and Mr. C. A. Grasselli, president, and his staff of superintendents were instrumental in showing everything in the works. None of the chemists will forget the pleasant little lunch which awaited them in the company's office.

Route No. 5 was of interest to iron works chemists, and comprised the Cleveland Rolling Mill and the Blast Furnace department and mill of the Union Rolling Mill Co. It was in charge of Mr. F. E. Hall.

The party left the Square at 1:30 P.M. Monday and proceeded first to the Crescent Sheet and Tin Plate Co.'s Works on Bessemer Avenue, near the N. Y. P. & O. R.R. This company employs two hundred men and has a capacity of thirty tons per day of sheet iron and tin plate. The plant is new, having been in operation about one year, and is fitted up with all the latest improvements in boilers, engines and all machinery, including an electric plant for lighting, and operating the electric cranes for handling rolls and heavy materials.

From here the party proceeded to the Emma Blast Furnace at the intersection of the N. Y. P. & O. and C. & P. Railroads. This furnace is operated by the Union Rolling Mill Co., whose rolling mills were visited later. The furnace department employs one hundred men and has a capacity of two hundred tons of pig iron daily. The plant is modern in every respect, has three blowing engines and three brick hot blast stoves. The company's chemical laboratory is located at the furnace plant and is in charge of Mr. Frank E. Hall.

The next place visited was the rolling mill of the same company, situated some distance farther up the C. & P. R.R. Here are employed about 350 men, the daily product of the works being about 150 tons of merchant iron. No steel is made, the company making a specialty of high grade wrought iron.

After inspecting this plant the party proceeded to the large works of the Cleveland Rolling Mill Co. This works is the largest in the city. The Bessemer Steel plant has a capacity of 1,000 tons daily, about seventy-five per cent. of which is made up into finished products, consisting of rails, shafts and wire, in the various departments of the company's works. In all about 3.500 men are employed.

One blast furnace is located at this plant. The company's two larger furnaces are located about three miles farther down on the N. Y. P. & O. R. R., from which place "direct metal" is run to the converters, the molten metal being carried this distance over the N. Y. P. & O. R. R.

The chemical laboratories of the company are in charge of Mr. Chaddock. Ten chemists are employed.

Route No. 8, Adelbert College and Case School of Applied Science were appointed for Monday evening Dr. Gruener, instructor of chemistry in Adelbert College, was absent on his vacation, and Mr. H. L. Payne, a graduate of the first chemistry class in Case School, was appointed to head this excursion.

The new physical laboratory of Adelbert College excited the greatest admiration. The chemical laboratory lacked its most interesting feature—Dr. E. W. Morley.

At Case School the visitors saw the marks of an active and well equipped institution for the study of practical applied science. The entertainment of the evening, of course, was Dr. Mabery's talk on "Petroleum."

Route No. 9 was to the Steel Works at Lorain, O. The trip was in charge of Mr. Hugo Carlsson, chief chemist of the Johnson Co.

These works occupy about eighty-six acres of land lying along the Black river, two miles south of Lorain. The plant was first put in operation April 1, 1895. Their finished products are billets and special rails for street railways. The plant consists of the Bessemer department, blooming mill, shape mill, engine and boiler houses, etc. Plans for the erection of six blast furnaces have been completed and work will begin on their erection soon.

The engine house contains the blowing engine for the Bessemer department; this was made by the Southwark Company, Philadelphia. It is a horizontal double expansion engine with blowing cylinder sixty inches diameter and sixty inches stroke. In the same building are the dynamos and straight line engines which furnish power for the Johnson Electric Railway between Lorain and Elyria. There are two boiler houses containing National Water Tube Boilers with Murphy Automatic Stokers, the combined capacity of the two batteries being about 6,000 horse power. The feed water is heated and purified before it enters the boilers. Gas for the heating furnaces is furnished by a plant of Duff gas producers. Four ten-foot cupolas melt the pig metal, and there are two eight-foot cupolas for spiegel. The converting department contains two ten ton vessels. Ingot molds are arranged on small cars in pairs. There is no casting pit. The ingots are transferred from the converter house to the soaking pits, in which they are kept until ready for rolling. The blooming mill is drived by a very powerful reversing engine, built by the Galloways, Manchester, England. It has double cylinders each fifty-five by sixty inches. The shape mill is driven by two engines, also of the Galloways' make. The heating furnaces are provided with two cranes, one for charging and one for drawing.

An important feature of the works is the special machinery for straightening rails. The laboratory occupies a two-story brick building, and contains a 250,000 pound Olsen testing machine.

THE RECEPTION BY THE CHAMBER OF COMMERCE.

The various hosts who had vied with one another in extending courtesies and hospitalities to the visiting chemists while in Cleveland, not being satisfied with the royal welcome which they had already given, tendered their guests a most delightful reception in the rooms of the Chamber of Commerce, Tuesday evening, Dec. 31. We quote from a Cleveland paper the following description of the elaborate decoration of the rooms:

"The decorations were to a certain extent paradoxical, being emblematic of both summer and winter. The walls of the ceiling were draped with holly, heavily laden with red berries. This drapery came down to within a few feet of the floor, where it was met by banks and screens of palms and other tropical plants. This apparent paradox was a pretty tribute to the various sections of the country, north and south, from which the guests came.

The floral designs added to the beauty of the scene. One, a large shield of white, studded with roses, bore the following inscription :

'Welcome, 1895—American Chemical Society.'

In the center of the assembly room, on a table, stood an immense design which was a tribute to Dr. E. W. Morley and took the form of a reference to his great genius in determining the atomic weight of oxygen. It was a huge balance erected on a base of American beauty roses. From the arms of the balance hung globes of white flowers. On one in purple was the simple capital letter 'O,' representing oxygen, and on the other the purple figures '15.879,' the atomic weight of oxygen."

On entering the Chamber the guests were welcomed by the Reception Committee, and introduced to the Cleveland gentlemen who were present. From early in the evening until midnight the visiting chemists had the pleasure of meeting in social intercourse those who had already done everything in their power to welcome and entertain the American Chemical Society, and to furnish them opportunities for a successful meeting.

During the evening the Chamber of Commerce Musical Club and the Schubert Mandolin Club rendered various choice selections, which were enthusiastically received. The evening was also enlivened by the humorous recitations and impersonations of Mr. J. E. V. Cooke.

Refreshments were served during the evening in the committee room, and it seemed as though nothing was wanting to make the occasion one long to be remembered. To cap the climax, however, and to show their appreciation of one of Cleveland's most distinguished scientists, a message of greeting and complimentary reference to his labors in determining the atomic weight of oxygen, was sent by cable to Dr. E. W. Morley, who is spending the winter in Europe.

Some of the chemists were obliged to leave on early trains and were thus unable to enjoy the whole of the evening. But they, as well as those who remained, took with them the pleasantest recollections of their visit to Cleveland, and the Twelfth General Meeting of the American Chemical Society.

Erratum.—Page 32, sixth line from bottom of page *for* sixty-three per cent. *read* sixty-three hundredths of one per cent.

Issued with April Number, 1896.

Proceedings.

COUNCIL.

The Council have approved the nomination of Edward Hart as Editor for 1896.

CHANGES OF ADDRESS.

Bloomfield, L. M., 1239 Harrison Ave., Cleveland, Ohio.
Furman, H. Van F., Room 118, Boston Building, Denver, Col.
Koebig, Dr. Julius, 306 Market St., San Francisco, Cal.
Pemberton, H., Jr., 1008 Clinton St., Philadelphia, Pa.
Phillips, Francis C., P. O. Box 126, Allegheny, Pa.
Sherman, H. C., Columbia University, New York City.
Spencer, G. L., 134 Rich Ave., Mt. Vernon, N. Y.

ADDRESSES WANTED.

Bachman, Irving A., formerly of Augusta, Ga.
Jones, Dr. Walter, formerly of Lafayette, Ind.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The annual meeting was held January 9, 1896, and was called to order by the President, Charles E. Munroe, at 8:00 P. M.

The following persons were elected to membership: Messrs. E. W. Magruder, C. C. Moore, and E. C. Wilson.

The publication of Bulletin No. 9 was announced and arrangements reported by a committee for a social meeting to be held in February.

The reports of the Treasurer and Secretary were read and adopted, after which the election of officers for the ensuing year was held with the following result:

President—E. A. de Schweinitz.

Vice Presidents—W. D. Bigelow and W. G. Brown.

Treasurer—W. P. Cutler.

Secretary—A. C. Peale.

Additional Members of the Executive Committee—Charles E. Munroe, V. K. Chestnut, F. P. Dewey, and H. N. Stokes.

The first paper of the evening was read by H. W. Wiley on a "Steam-Jacketed Drying Oven." "In order to surround the drying space of an oven entirely with steam, the door of an ordinary steam-jacketed drying oven is made with double walls, into which the steam from the oven is conducted by two metal flexible tubes inserted at the top and bottom of the door. They are so arranged as not to interfere with opening the door. By this method the entire drying space of the apparatus is surrounded with steam, easily securing a constant and even temperature.

The temperature is regulated by a pressure gauge in which the steam, by acting on a column of mercury, cuts off the gas when a given pressure is reached. A steam pressure of two inches will cause a temperature of about 102° in the drying space of the oven. By setting the gauge at any position desired, the temperature can be regulated, when steam is used, to read from the boiling point of water up to 105°. For other temperatures other liquids can be used. For instance, alcohol, or amyl alcohol for still higher temperatures, and so on. Ether cannot be employed with safety on account of the danger of explosion in case of leakage."

Dr. Wiley exhibited the drying oven in actual operation.

The second paper, also by Dr. Wiley, was on the "Heat of Bromination of Oils." "The method of determining the heat of bromination of oils, as proposed by Hehner and Mitchell, in a recent number of the *Analyst*, is very difficult to work from the meager directions given by the authors. The especial difficulty in the process is in handling the liquid bromine in quantities of one cc. at a time. I find that the process is made practicable by dissolving both the oil or fat and the bromine in chloroform, in which condition the bromine solution is easily handled by means of a special pipette.

In order to make a number of analyses of the same sample, five grams of the fat may be dissolved in chloroform and the volume completed to fifty cc. Ten cc. of this solution will contain one gram of the fat. In like manner five cc. of bromine may be dissolved in chloroform and the volume completed to fifty cc., or larger quantities in the same proportion may be used. The gradual evolution of hydrobromic acid from a mixture does not interfere with the analytical process, as the amount of bromine used is always largely in excess. Ten cc. of the bromine solution containing one cc. of the liquid bromine are used for each ten cc. of fat solution.

The pipette for handling the bromine solution is so arranged as to be filled by the pressure of a rubber bulb, thus avoiding the danger of sucking the bromine vapor into the mouth. The solution is poured upon the chloroform solution held in a long narrow tube, in which a delicate thermometer, capable of being read to tenths of a degree, by means of a magnifying glass, is placed. This tube is held in a large cylinder, from which the air can be removed, thus affording a good insulation in respect to heat.

The determinations should be conducted in a room where the temperature is as constant as possible and the pieces of the apparatus should be exposed to the open air for at least half an hour after completing one determination before beginning another, in order to be restored to the standard room temperature. Duplicates usually agree within one or two-tenths of a degree, though sometimes the variations are greater.

The ratio of the heat of bromination to the ordinary number must be established for each system of apparatus employed. The heat of bromination of various oils was determined by the method and apparatus described above, and the process seems to be one of considerable analytical value. For exact scientific purposes, calorimetric measurements of the degree of heat produced must be made."

Discussion was by Messrs. Warder, Freeman and Munroe.

Professor Charles E. Munroe then made some remarks upon the "Corrosion of Electric Mains." He exhibited sections of electric light cables in which the lead coating had become so corroded that in some places the interior conductor was exposed, while at others the cable was coated with nodular earthy-looking masses. The cables were parts of and arranged on the three wire system, which carried a direct current of 110 volts on each wire, and which had been laid underground in the upper compartment of a terra cotta conduit. The corroded main was a branch in an alley. The principal main in the street was not attacked in the least. Analysis showed the incrustation to contain nitrate, chloride, carbonate, oxide of lead, water and a trace of organic matter. Surrounding the alley were stables, and the author found in the salts in the soil produced by the excreta all the necessary materials and conditions for effecting chemical corrosion *per se.*, without resorting to any electrolytic theory.

Dr. Wiley, in discussing the paper, said he thought there might have been a denitrifying process.

Professor Munroe said there could have been no constant moisture present, that is, there was no submergence, but there must have been water passing through the conduit.

CINCINNATI SECTION.

The Section met in regular session Saturday evening, February 15, 1896. Vice President Martin presided.

Dr. Alfred Springer read a paper on "The Characteristics of Illuminates," and exhibited a photograph of the bones of the hand made by means of the Roentgen X rays. The picture was kindly loaned for the purpose by Mr. G. W. Zwick, of Covington, Ky., who had recently brought it from Germany.

"Notes on Helium and Argon" was read by Professor T. H. Norton.

Dr. S. Waldbott showed how the value of litmus paper as an indicator could be enhanced. His method was to use a capillary pipette instead of an ordinary stirring rod, and to hold the point of the pipette containing a drop of the solution upon the litmus paper; a bright red spot would be seen at the point of contact, even in very dilute acid solutions. The Doctor's paper on "The Assay of Ipecac," announced for the evening, was postponed till next meeting.

NORTH CAROLINA SECTION.

On February 22nd about a dozen chemists met in the office of the Experiment Station in Raleigh to organize the North Carolina Section. The following officers were elected:

President—F. P. Venable, University of North Carolina, Chapel Hill.

Vice President—Charles E. Brewer, Wake Forest, N. C.

Secretary and Treasurer—W. A. Withers, Raleigh, N. C.

The following papers were read:

"Absorptive Power of the Soil for Bases and Its Relation to Fertility," by Prof. Withers.

"A Study of the Zirconates," by Dr. Venable and Mr. Clarke.

"Notes on the Reduction of Methylenedi-*o*-*p*-*m*-nitraniline," by Dr. Baskerville.

NEW YORK SECTION.

The regular meeting of the New York Section was held at the College of the City of New York, on Friday evening, March 6th, at 8:30 o'clock. Professor P. T. Austen in the chair.

The following papers were read:

"The Cassel-Hinman Gold and Bromine Process," by P. C. McIlhiney."

"The Specific Gravity of Glue Solutions," by E. R. Hewitt.

"Investigations in the Chemistry of Nutrition," by Dr. W. O. Atwater.

Mr. McIlhiney enumerated the advantages of bromine over chlorine in the gold extraction process as (1) greater solubility of bromine, as three and two-tenths per cent. against 0.76 per cent.; (2) lesser oxidizing pywer, whereby the iron pyrites is less acted upon; (3) greater solvent power for gold.

The bromine is recovered by distillation with live steam in stone tanks, after addition of sulphuric acid and an oxidizing agent.

The process is especially adapted to low grade telluride ores, which have not hitherto been profitably worked.

Mr. Cassel, being present, was asked to what extent the process had been worked, and whether ores containing sulphides could be treated. He replied that fifty tons *per diem* had been treated since January 1st, and the capacity was to be increased; that ores containing small amounts of sulphides had been successfully treated, using very weak solution of bromine, and eighty per cent. of the bromine had been recovered; but it was best to roast sulphide ores. The cost, including roasting, was $1.75 per ton.

Mr. Hewitt, in his work on the "Specific Gravity of Glue Solutions," had obtained his results from experiments on all grades of glue from the best photographic gelatine, to the darkest and poorest grades in the market.

He found the expansion of glue solutions to be the same as water alone; that the specific gravity of glue containing water was less than in the dry state; that the hydrometer could not be used in solutions containing over sixty-five per cent., and that the quality of the glue had no effect on the specific gravity of the solutions.

He concludes that there is a series of distinct chemical combinations of glue with water.

In the discussion of the paper, Dr. Horne asked if the specific gravity of a glue solution could be determined by dropping it into some solution of known density, not acting on the glue solution.

Mr. Hewitt replied that this method had been tried, using xylol, chloroform, and some other liquids, but the results were not as satisfactory as could be obtained by the hydrometer.

The presence of Dr. C. B. Dudley, President of the Society, was then announced, and Dr. Dudley addressed the meeting in part, as follows:

"*Gentlemen of the New York Section:* It has been a rare pleasure to attend this meeting of the New York Section, and I would like to congratulate you on one or two points. First, the advantage that comes to you from being able to meet together, read papers, shake hands and dine together. I am so far away from the chemists that it does me good to meet and shake hands with a chemist. In the early days of the Pittsburg Society I tried to meet with them and have been present on many enjoyable occasions, but having joined the Society when there was only a New York Section, I have felt at home with you and have wished I could meet with you oftener.

"Another thing on which I wish to congratulate you. Our General Secretary informs me that we have a good round thousand now in our membership. There are those of you who have stood by the Society when it was not as prosperous as it is now, who can appreciate this.

"Now as to what is to be done in the field of our labors. My daily work, or a great part of it, is with iron and steel, and if I could, I would give all my time to the study of pig iron.

"There are many problems yet to be solved in regard to it, and of which a great deal might be said, but as there are other papers to come before you this evening, I will not detain you longer. I am very glad to have been able to meet with you."

Dr. W. O. Atwater was then introduced, and after giving a synopsis of the work which had been done in other countries, especially in Germany, on the chemistry of food and nutrition, he described the progress which had been made in this country, beginning with the early work of Professor Baird, then of the Smithsonian Institute, who gave the first impulse to this work by his studies of the food value of a number of varieties of fish. He then passed to a description of the work recently done under his direction and that now in progress in determining the heats of combustion, or fuel values of food. He said that we know the laws of conservation of energy hold good in the living organism, but we do not yet know *how* they hold good. We must study these things in the living organism, and for this paper a respiratory calorimeter has been constructed at Middletown by which the experimental determination of heat of radiation, energy of food consumed, etc., is to be obtained. A man had been kept in this apparatus for four days, and it was expected to arrange to extend the experiment to a week or even several weeks.

Eight attendants were required to run these experiments.

Dr. Dudley asked whether Professor Atwater had used a current of oxygen instead of potassium chlorate in his experiments on the heats of combustion of foods, and stated that he had used the oxygen with very satisfactory results in determinations of calorific value of coal.

Dr. Dudley also asked whether the quality of the fat of animals was dependent on the food.

Professor Atwater replied that the fat formation is a function of both the organism and the food.

On motion of the Secretary, a vote of thanks was passed to Professor Atwater for his interesting report on the progress of the chemistry of nutrition.

Professor Breneman moved that a committee be appointed to make a report at the next meeting on the feasibility of organizing a chemical club from the members of the New York Section. Seconded and carried.

The Chair appointed Messrs. Breneman, McMurtrie, and Hallock.

The Librarian announced the receipt of a bequest from Dr. A. A. Fesquet, of two microscopes and accessories. The Chair directed that a suitable recognition of the gift be made.

RHODE ISLAND SECTION.

The regular meeting of the Rhode Island Section was held at Providence, Thursday evening, Feb. 13, 1896. Mr. Chas. S. Bush in the chair.

A paper was read by Mr. Charles E. Swett. Subject, "Ultramarine."

The reader presented the results of a few experiments he had performed upon ultramarine, with some of the more common reagents.

The March meeting was held on the 19th inst., at Providence. Chairman C. A. Catlin, presiding.

Mr. Walter E. Smith read a paper upon "The Origin of Petroleum."

In brief, the paper was as follows:

The theories given for the origin of petroleum are in general divided into three classes:

1. The chemical theories advanced by Berthelot and Mendeléeff, that water on metallic carbides forms acetylene, which is further changed.

2. The theory that it is indigenous to the rocks in which it is found.

3. The theory that it is a distillate formed from highly organized substances.

Proceedings.

COUNCIL.

The Council has decided to hold the summer meeting at Buffalo, August 21 and 22.

NEW MEMBERS ELECTED MARCH 26, 1896.

Brown, Thomas, Jr., M.S., Princeton, N. J.
Danner, W. E., 441 Green St., Philadelphia.
LaWall, Charles H., 305 Cherry St., Philadelphia.
Nagelvoort, J. B., 3237 Michigan Ave., Chicago, Ill.
Sprout, Louis P., Scotia, Pa., P. O. Benore.
Stewart, Dr. Andrew, 1420 Q St., N. W., Washington, D. C.
Wagner, John R., Drifton, Pa.

ASSOCIATES ELECTED MARCH 26, 1876.

Caldwell, Thomas O., Agr. Exp. Sta., Bozeman, Mont.
Flowers, John, Agr. Exp. Sta., Bozeman, Mont.
Pilgrim, Heber B., Lafayette College, Easton, Pa.
Sieb, Peter, Agr. Exp. Sta., Bozeman, Mont.
Twitchell, Mayville W., 709 8th St., N.E., Washington, D.C.
Walter, Charles Albert, 506 South 5th St., Champaign, Ill.

CHANGES OF ADDRESS.

Barton, G. E., care Whitall, Tatum & Co., Flint Glass Works, Millville, N. J.
Benjamin, Dr. Marcus, Smithsonian Institute, Washington, D. C.
Berry, W. G., 26 Whitehall St., N. Y. City.
Breyer, Theo., P. O. box 112, Peoria, Ill.
Brown, H. F., 113 West Central St., Natick, Mass.
Fields, J. W., Stillwater, Okla.
Johns, John, 306 Toone St., Baltimore, Md.
Kelley, J. H., 26 Snell Hall, Univ. of Chicago, Chicago, Ill.
Lloyd, Rachael, care R. L. Lloyd, Lansdowne, Pa.
Low, A. H., P. O. drawer 1537, Denver, Colo.
Maury, George P., care Edgar Thompson Steel Works, Braddock, Pa.
Nickel, Herman L., care N. K. Fairbank Co., St. Louis, Mo.
Pomeroy, Charles T., 190 Mt. Pleasant Ave., Newark, N. J.
Rosengarten, F. H., care Photographic Society, 10 So. 18th St., Philadelphia, Pa.
Steiger, Geo., 1425 Corcoran St., N.W., Washington, D. C.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

A regular meeting was held February 13th, 1896. As the meeting was devoted mainly to social purposes and the inauguration of the newly elected president, Dr. E. A. de Schweinitz, it was held at the rooms of The Washington Down Town Lunch Club. After the transaction of necessary business a lunch was served which was enjoyed by thirty-one members. The following persons were elected to membership: Clinton P. Townsend, S. S. Voorhees, and Dr. F. K. Cameron.

The Presidential address before the Washington Section was delivered by the retiring President, Professor Charles E. Munroe, at a special meeting held Friday, February 21, the subject being "The Development of Smokeless Powders." The lecturer sought to show that the necessity for a high-power, smokeless propellent had been created by the mechanical perfection to which ordnance had attained and the precision of the weapons and the instruments by which they were directed; that the possible production of such propellent was dependent on the discovery of guncotton, nitroglycerol, and certain nitro-substitution compounds, and the improvements in their manufacture; that the possibility of producing uniform and reliable propellents was dependent on the invention of pressure gauges and velocimeters; and that the possibility of their economical production was dependent on the invention of mechanical mixers and formers applied in other arts. In a historical résumé it was shown how very recent most prior inventions and discoveries were, and it was pointed out that a very large proportion of the inventions were made by American scientific men.

The many smokeless powders manufactured or prepared were then described or enumerated and classified into mixtures of different cellulose nitrates with oxidizing agents; mixtures of soluble or insoluble cellulose nitrates with oxidizing agents; mixtures of soluble or insoluble cellulose nitrates with nitroglycerol; mixtures of cellulose nitrates with nitro-substitution compounds; and pure cellulose nitrate powders; and the methods of manufacture were briefly stated.

The lecturer then related his own experience in inventing a smokeless powder. Recognizing at the outset the necessity for the closest approximation to absolute chemical and physical uniformity in a high-powered powder, and being familiar with the difficulty of securing such constancy in a physical mixture, he set about producing a powder from carefully purified cellulose nitrate of the highest degree of nitration. This was the first and only attempt made, so far as the lecturer was aware, to produce a powder which consisted of a single substance in its pure state.

A factory was erected at the Torpedo Station, prior to his resignation of his position there, and the powder manufactured was proved at Indian Head by Ordnance Officers of the Navy. Secretary Tracy said of this powder, "Report of the Secretary of the Navy, 1892, page 25." "It became apparent to the Department early in this administration that unless it was content to pass behind the standard of military and naval progress abroad in respect to powder, it must take some steps to develop and to provide for the manufacture in this country of the new smokeless powder, from which extraordinary results had been obtained in Europe." With this object negotiations were at first attempted looking to the acquisition of the secret of its composition and manufacture. Finding itself unable to accomplish this the Department turned its attention to the development of a similar product from independent investigation. The history of these investigations and of the successful work performed in this direction at the Torpedo Station has been recited in previous reports. It is a gratifying fact to be able to show that what we could not obtain through the assistance of others we succeeded in accomplishing ourselves, and that the results are considerably in advance of those hitherto obtained in foreign countries."

The conditions that a smokeless powder should fulfill and the tests prescribed by the lecturer were then set forth, and in closing he pointed out that the powder was now developed to a higher degree than the gun and that changes in the latter to render it more efficient were being considered by ordnance experts.

CINCINNATI SECTION.

The Section met in regular session, Tuesday, March 17, 1896. President Twitchell presided.

The discussion of "The Scientific Concepts of Etidorhpa" was announced for the evening. The popularity of the book was evidenced by the presence of many friends of the author and of the other members of the Section.

Dr. Alfred Springer read extracts from the book and took issue with the author on some of the statements. Prof. Lloyd re-affirmed his belief in the theories advanced and referred the Doctor to the preface to the author's edition, in which he had stated he would decline "to make any subsequent comments on the work." The Professor then read three chapters in the original manuscript, which had been omitted from the published work. He now regrets the omission, as the continuity of the narrative is somewhat impaired thereby.

RHODE ISLAND SECTION.

The regular meeting of the Rhode Island Section was held at Providence, Thursday evening, April 16, 1896, Chairman, Charles A. Catlin, presiding.

Mr. Charles S. Bush read a paper on "Petroleum Products." The following is an outline of the paper:

1. Discovery of petroleum.
2. Brief history of the petroleum industry in the United States.
3. Outline of the distilling and refining process now in general use in the United States.
4. The importance of petroleum as a means of reducing friction to a minimum.
5. New methods compared with old ones, especially referring to "petroleum products" used for lubricating purposes.

NEBRASKA SECTION.

The regular meeting of the Nebraska Section was held at the University of Nebraska, on Tuesday evening, March 31, at eight o'clock.

The president being absent, Mr. Samuel Avery was elected chairman *pro tem.*, and called the meeting to order.

The following papers were read :

"Recent Work on the Röentgen Rays," by Prof. D. B. Brace, of the Department of Physics, University of Nebraska.

"Report on Argon," by Miss Rosa Bouton.

"Calcium Carbide and Acetylene," by Dr. John White.

Prof. Brace exhibited some Crookes' tubes prepared in his laboratory, made a general statement of the manner in which these were prepared and used, of the effect of the X or Röentgen rays, and exhibited some photographs taken by their use. Of these one was of special interest; it represented a shadograph of a metal object taken by the cathode and anode rays. There was no appreciable distinction between them.

Miss Bouton's paper gave a very thorough and clear account of argon, from the very earliest experiments of Lord Rayleigh on the density of nitrogen down to and including the present state of our knowledge of argon, its chemical and physical properties.

Dr. White exhibited a specimen of calcium carbide, which had been prepared in the electrical laboratory of the University, gave a brief historical statement of the carbides in general, and of their use in the preparation of acetylene. He then prepared some acetylene by treatment of the carbide with water, and by burning the gas under proper conditions showed how it may be used as an illuminant. He followed this by a short lecture, in which the economic use of acetylene as an illuminant was dealt with, laying special stress upon its advantages and disadvantages.

Owing to the lateness of the hour, Dr. White's paper on "Metallic Suboxides" was postponed.

At the business meeting which followed, Mr. E. C. Ellioet and Miss Marietta Gray were elected members of the Section.

NEW YORK SECTION.

Minutes of the meeting of April 10.

A report was made by the chairman of the committee appointed to consider the organization of a chemical club in New York. Out of eighty-two replies already received, sixty were unconditionally in favor of the project.

It was further stated that as there had evidently been some misunderstanding as to the intended membership, it should be known that there is no intention of limiting the membership to any section of the chemical fraternity, but to include chemists and chemical manufacturers generally.

Dr. Albert R. Leads read a paper on "Standard Prisms in Water Analysis, and the Valuation of Color in Potable Waters."

In the discussion of Dr. Leed's paper, Prof. Birchmore explained an arrangement of adjustible colored prisms projecting inside a glass cylinder, one over the other, by which the Nessler reagent colors could be matched and recorded. The cylinder is to be filled with a liquid having the same refractive index as glass; oil of juniper was mentioned as suitable; and the record is made by readings on the milled heads of the screws by which the overlapping of the prisms is regulated.

Dr. Leeds moved that a committee be appointed to unify the methods of color comparison and report upon a standard of measurement of color in potable waters.

Prof. McMurtrie thought that such committee should be appointed by the council, and that the secretary should communicate the resolution to the President of the Society.

Dr. Leeds' motion, as amended by Prof. McMurtrie, was seconded and carried.

A paper was read by C. L. Speyers on "Matter and Energy."

Dr. E. G. Love exhibited some fine photomicrographs of starches.

Dr. L. Saarbach exhibited and described an improved form of "Laboratory Temperature Regulator," which he had found sensitive, reliable, adjustable, and easily taken apart for cleaning.

Issued with June Number, 1896.

Proceedings.

COUNCIL.

Prof. H. H. Nicholson, Lincoln, Neb., has been elected a member of the Council, to take the place left vacant by the election of Dr. C. B. Dudley to the presidency of the Society.

The Council has voted to accept the invitation to hold the winter meeting at Troy, N. Y., on Tuesday and Wednesday, December 29 and 30.

The New York Section has asked that a committee be appointed to unify the methods of color comparison and report on a standard for measurement of color in potable waters. The Council has agreed to the formation of such a committee and named the following persons to act as members: A. R. Leeds, Wm. P. Mason, Thomas M. Drown.

NEW MEMBERS ELECTED MAY 11, 1896.

Bowman, J. W., Green Island, N. Y.
Hunziger, Dr. Aug., care Weidman Silk Dyeing Co., Paterson, N. J.
Yates, J. A., Williamsburg, Ky.

ASSOCIATES ELECTED MAY 11, 1896.

Meade, Richard K., Longdale, Va.
Pilhashy, Benjamin M., 1058 Cutter St., Cincinnati, O.

CHANGES OF ADDRESS.

Dodge, F. E., 316 Bowne Ave, Flushing, N. Y.
Hays, Joseph A., 147 So. 18th St., Pittsburg, Pa.
Hopkins, Cyril G., 409 W. Main St., Urbana, Ill.
Lord, N. W., 338 W. Eighth Ave., Columbus, O.
Peale, A. C., box 2043, Station A, Philadelphia, Pa.
Power, Frederick B., 535 Warren St., Hudson, N. Y.
Shepherd, Frank I., Kyle, Ohio.
Stillwell, J. S., box 3015, N. Y. City.
Tonceda, Enrique, care Troy Steel Co., Troy, N. Y.

ADDRESSES WANTED.

Gallaher, Phil. C., formerly of Leadville, Colo.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

The regular meeting of the Section was held Wednesday evening, April 15th.

Dr. S. Waldbott presented a paper on "The Assay of Ipecac," in which he outlined the various methods for the alkaloidal assay of crude drugs and gave some results obtained by applying the Lloyd method for the assay of fluid extracts, to the determination of emetine in ipecac root; with some slight modification, Dr. Waldbott thinks good results may be obtained.

In a paper on "The iodoso- and iodo-compounds and iodonium bases, Dr. John McCrae gave an interesting account of some of the work he had done on these compounds, under the instruction of Victor Meyer.

NEW YORK SECTION.

The New York Section held its usual monthly meeting in the chemical lecture room in the College of the City of New York on Friday evening, May 8, with about fifty members present, Dr. Peter T. Austen, presiding. In response to inquiries regarding the progress made by the committee appointed to canvass the matter of the organization of a chemical club, Prof. Austen stated that in accordance with the instructions given, it had increased its numbers to fifteen and had held several meetings, to one of which the members of the New York sections of the American Chemical Society and of the Society of Chemical Industry, as well as manufacturers and gentlemen interested in the science and art of chemistry, business men and friends of chemistry were invited. The meeting was full and enthusiastic. The committee was instructed to increase its number to fifty or more and to push the organization of the club as rapidly as possible. The committee had held another meeting and added a large number of names of prominent chemists, manufacturers, and business men to the list. The general opinion seems to be that the initiation fee should be fixed at $25, and yearly dues at $25. It is the intention, while in no way hampering or restricting the evolution of the Chemical Club, which many of the more enthusiastic supporters of the movement predict, to start the club in a conservative and economical way, and not to exceed the pecuniary limit which shall be decided upon after careful deliberation. It appears that there is not in existence in this or any foreign country any real chemical club, as differentiated from a chemical society. It is believed that the science and art of chemistry furnish so much that is characteristic that a chemical club may easily be made a unique organization. The members of the committee of fifteen are Prof. A. A. Breneman, Dr. A. P. Hallock, Prof. Peter T. Austen, Dr. W. McMurtrie, Prof. Morris Loeb, Prof. C. A. Doremus, Dr. E. R. Squibb, Dr. J. H. Wainwright, Mr. A. H. Mason, Mr. S. W. Fairchild, Mr. W. H. Nichols, Mr. W. J. Matheson, Mr. T. F. Main, Prof. A. H. Sabin, and Dr. C. F. Chandler.

Dr. A. R. Leeds, of Stevens Institute, read a paper on the "Bacteria of Milk Sugar." The author finds that the morphology, classification, physiology, and botany of bacteria are so rudimentary and unsatisfactory that the most valuable methods of bacteriological investigation are still of a chemical nature, and the advances to be made in the near future are to be looked for mainly on the chemical sides of the subject.

The author was interested to note in the progress of his work that precipitated zinc hydroxide, which is generally considered amorphous or gelatinous, is really crystalline.

Dr. H. W. Wiley, of the United States Department of Agriculture in Washington, offered a paper entitled "Recent Advances in Milk Investigations." In the absence of the author the paper was read by Dr. William McMurtrie. It treated of the bacterial theory of milk decomposition, the composition of woman's milk as compared with cow's milk, and the relative value of the two for infant food, and of the commercial standards which should be fixed for the milks sent to the city markets.

The author reviewed the work of Söldner regarding the proteid content of human milk, and quoted the figures given by authority for the average composition of human milk, as follows:

	Per cent.
Proteids	1.52
Fat	3.28
Sugar	6.50
Ash	0.27
Citric acid	0.05
Undetermined	0.78
Total dry substance	12.40

The undetermined substances, 0.78 per cent., are mostly nitrogenous bodies not generally found in cow's milk, and for this reason cow's milk can never be so diluted or altered as to properly supply the natural nutriment of the infant.

Söldner follows the method of Munk for determination of proteids, regarding as non-proteid matter those nitrogenous bodies not precipitated by tannin in presence of common salt. In woman's milk these amount to nine per cent. of the total nitrogenous constituents, and in cow's milk to about six per cent.

The author then discussed the view of Bechamp that milk derived from healthy animals is capable of spontaneous alteration, which consists in the development of lactic acid and alcohol and the development of curds in those milks which contain caseinates produced by the precipitating action of the acids formed. Oxygen and the germs present in the air are held to have nothing to do with this alteration of the properties of milk. The general conclusion reached is that microorganisms, such as vibriones and bacteria, are developed by a natural evolution from the microzymes, even in milk which has been boiled.

The surprising results of Söldner and Bechamp should lead to new studies of bacterial action in milk. If it should prove true that milk contains autogenetic germs for its own change, and that by the development of these germs into vibriones and bacteria, the natural souring takes place, it will be necessary to change completely the common view respecting these processes.

The author further discussed the commercial standards for the composition of milk, declaring that the value of milk, both for butter and cheese making, should be gauged by its content of butter fat, denouncing the claim of dealers that any milk from a healthy cow should be sold without legal restriction, no difference what its content of fat may be, and recommending that the minimum standard for fat content of milk supplied for human consumption should be placed at three per cent. or higher.

Dr. Leeds considers that in judging of the figures of Söldner presented it is important to be informed of the conditions under which the samples for analysis were taken and the quantity used for analysis, particularly for the determination of such constituents as citric acid and the undetermined substances. Samples of woman's milk usually available are too small for such minute determinations. Regarding the content of proteids, the figures of Söldner do not vary widely from those previously found and reported. One hundred samples of woman's milk examined in New York gave an average of less than two per cent., with variations of 0.75 per cent. to 4.75 per cent. The only explanation of the very low figure of Söldner is that only partial secretion was available. The figure 1.52 given is not surprising.

That the various bodies secreted from the blood should be present is generally accepted. Variations in the composition of the milk, due to emotional influences, such as nervousness, excitement, fatigue, fright, anger, etc., are well known.

The fat and total solids given in the analysis are surprisingly low.

Dr. Eccles questioned the declaration that modified cow's milk was not a proper food for infants. Constant experience, forced by necessity, shows that it supplies excellent nutrition for infants.

Prof. Marston Bogert, of Columbia College, read a paper on "Normal Heptyl Thiocyanate."

The steps followed by the author in preparation of heptyl thiocyanate are as follows: Production of heptyl alcohol from oenanthol by reduction with zinc dust and acetic acid, conversion of the heptyl alcohol into the bromide, and addition of the bromide to boiling alcoholic solution of potassium thiocyanate. The yellow oil finally obtained washed free from potassium thiocyanate, dried with calcium chloride and distilled, all passed over between 230° and 234° C.

Normal heptyl thiocyanate is a colorless, mobile liquid, having a slightly alliaceous but rather pleasant odor and a specific gravity of 0.931 at 15° C.

Dr. Austen exhibited an apparatus for lecture demonstration of the properties of the heavier gases.

WASHINGTON SECTION.

A regular meeting was held Thursday, March 12th, 1896, with President Dr. de Schweinitz in the chair. There were thirty-five members present, and Dr. Andrew Stewart was elected to membership.

Mr. F. P. Dewey read a paper on "The Refining of Lixivating Sulphides." Dr. Dewey's paper reviewed the leaching process and the treatment of sulphide precipitates produced. He described the sulphuric acid process of treating the sulphides, in which they are treated in strong sulphuric acid to convert the sulphides into sulphates, after the charge is treated with water, the silver precipitated by copper and melted, the copper sulphate crystallized. In the 1894 run of the Marsac Refinery, 116,519½ pounds of sulphides, carrying 572,544.4 ounces of silver by the corrected assay were treated, and 574,623.26 ounces of silver were returned, showing a plus clean up of 2,073.81 ounces, or 0.36 per cent. 96.29 per cent. of the product was in the form of bars, averaging 999.4 fine in silver, no gold.

Professor H. W. Wiley and E. E. Ewell read a paper[1] on "The Determination of Lactose in Milks by Double Dilution and Polarization."

Professor H. Carrington Bolton read a paper on "Berthelot's Contributions to the History of Chemistry," reviewing his "Collection des Alchimistes Grecs," (Paris, 1887; 3 Vol. 4to), and his "La Chimie an Moyen Age," (Paris, 1893; 3 Vol. 4to), showing their scope, analyzing their contents and indicating the important changes in chemical history resulting from Berthelot's studies.[2]

In the discussion of Dr. Bolton's paper, Dr. Wiley referred to the fact that the Phoenicians, as early as 1200 years before Christ, became famous by reason of the remarkable dyes which they produced, and that they were derived from a colorless substance found in certain mollusks, which, when exposed on fibers to the light, turned green, then red and purple. He referred to the fact that on the continent of Europe many scientific men had also become famous in politics, and among them preëminently Berthelot and Virchow. Berthelot was at least one official chemist who had attained political distinction, and his career might be imitated with advantage to the public service by some

[1] This Journal, 18, 428.

[2] This Journal, 18, 466.

American scientists; and we should not despair of looking forward to the day when chemists should at least be members of the Cabinet, if not Presidents of the United States. He thought Berthelot was particularly well suited to write of the alchemists, because some of his views would do credit to the wildest vagaries of the alchemists, especially his notion that the art of the chemist in the synthesis of foods, would in the near future render the practice of agriculture unnecessary. But we should not criticise a great man because of his vagaries, and after all it may be true that insanity is the highest type of genius.

The topic of discussion for the evening was "Style in Chemical Books and Papers." Dr. Wiley opened the discussion by saying there are many problems that present themselves to authors of scientific work. Some of these are of vital importance, while others are mere matters of taste. Not having expected to discuss the question on this occasion, he would confine himself to the minor topics. He suggested that there should be some uniform systsm of abbreviation employed, and for his part preferred very much small letters without periods. The introduction of capital letters in abbreviations marred the appearance of a book, and appeared to be entirely unnecessary. He thought perhaps some abbreviation of common metric terms would prove advantageous; for instance, the writing of the words cubic centimeters repeatedly not only requires a great deal of space, but the repetition of the term becomes tiresome. Some short word might be used to represent this magnitude, as, for instance, cubics. It would be well for chemists to agree upon some such system, provided the system were rational and easy of application.

Another question which often arises is in regard to the agreement between the noun and the verb, as, for instance, should we say 100 grams of iron are, or 100 grams of iron is? Another minor point is in the writing of numerals; whether they should be written out or the Arabic numerals used. He has adopted the plan of writing out in full numbers below 100, and placing the Arabic numerals for 100 and above. This was an arbitrary division, however, which might well be changed if some agreement could be reached in regard to it.

It appears that most scientific writers are so eager to express the truth or fact which they wish to convey that they lose sight altogether of the style in which the expression is made, and, as a result, their sentences become involved, and their meaning far from clear.

Another point which merits discussion is in the use of proper names to indicate any apparatus or process known by the name of the inventor. He preferred in such cases, where the personal idea had been lost, to use no capital, but to write the name of the apparatus or process with a small letter, as, for instance, a gooch or an erlenmeyer. The same is true of materials or reagents with geographical adjectives, as for instance, german silver and canada balsam, both of which should be written with small letters, just as the French, without disparaging the great Emperor, write the name of the coin napoleon with a little n or as we write telford or macadam for the name of a road.

Chemists should be careful about "take." It is not elegant to say "take five grams and place in a dish." "Place five grams in a dish" is entirely sufficient. In one work on chemistry he found the author directing the analyst to "take twenty-five grams of Glauber salts" with a big g. "Weigh out" is inadmissable. We do not weigh out, nor in, nor on, nor under. We simply weigh. In measuring it is not necessary to say weigh, as the chemist knows enough to use the balance without specific directions. A typically unnecessary form of expression and one not impossible to find is "take barium chloride, weigh out five grams, dissolve in water and filter off the insoluble residue."

Above all, the scientific writer should avoid indulging in fine writing. Plain, unvarnished statement of fact in a clear, lucid manner is what we should strive for. An example of how not to write is the following:

"For not only does the soil make possible a very much greater profusion of land life than could otherwise exist, but it has also played an extremely important part in that long-continued never-ending, and sublime process of evolution whereby, as lands have insensibly changed into sea and seas into land, as mountains have risen so slowly and silently out of level plains as to spring their broad arches directly across wide rivers to the height of a mile and yet leave their course unaltered, as climates have changed from cold to warm or from wet to dry, both plants and animals in this great drama of the world action have been enabled to change, not simply their costumes, but, if the exigencies of the new scene demanded it, legs for fins or even abandon them altogether and crawl upon their bellies through the grass."

Professor Bolton said he thought one's grammar school education must have something to do with style in writing. Great labor is expended nowadays upon abstracts from foreign publications. He thought there should be a different method of treating them. The results might be presented without giving the steps by which they are reached. He thought that no one could depend entirely upon the abstracts, but have to refer to the original papers for details.

Professor Seaman said he was glad the subject was brought up; he thought some chemists had an idea that the English language is sacred, and that no changes should be made in it. This feeling must be met. He said that most persons read by words, and not by letters, and if a word has not the usual appearance to which we are accustomed, our first impression is that it is wrong, and hence he feared that no changes, however judicious, would seem agreeable. As to the agreement of collective nouns with verbs, Goold Brown concluded that the only principle to be followed is euphony. When the best grammarians cannot formulate rules, uniformity can hardly be expected. As to the use of small letters instead of capitals, the various changes that are going on in the language generally ought to be considered. The councils of biological societies have agreed that small letters should be used. Up to a few years ago specific names derived from proper names were begun with capitals, but now the small letters are used. As to the abbreviations used for weights and measures, he said no system had universal assent. Physicists and mechanicians have in use a long series of abbreviations for linear, areal and cubic measures. In three of the most important German chemical works, including the "Berichte," small letters are used, for the liters (l); for the grams (g); and for cubic centimeters (cc.), and he would be in favor of adopting these, but unfortunately the pharmacists and physicians who are endeavoring to introduce them into their arts, have agreed upon the capital G and small r for gram, and capital C and small c without a point between them for cubic centimeter. Remsen in his first edition used cc., g., and l. Which are chemists to follow? The French do not use habitually any abbreviations. Some chemists, unfortunately, have not adopted the new spelling.

Professor Clarke said that a friend who wished to become a journalist, had consulted a newspaper man, and the advice he received was simple—"Have something to say and say it." Sometimes the writer is not sure as to what he wishes to say, and he tries to say something else, and his writing becomes involved. Another fault which was observed, especially in those who have just returned from abroad, was that everything that has ever been written upon the subject is given in an article, and the discovery of the authors is either buried in the mass or occupies a very small place at the end of the article. He thought a logical order should be followed, and an effort should be made to state what is said, simply and clearly. He thought Steele's "Fourteen Weeks in Chemistry" was a model of bad style.

Professor Munroe said that so far in the discussion there was apparently very little difference of opinion. He read the following from an article in "Science." "If we hear a baby crying with two ears, are we to think it is twins?" as an example of style in a scientific article. He thought this illustrated Professor Clarke's remarks about having something to say and saying it. Professor Munroe thought that the question of style had to be considered from two standpoints: that of the manual or text-book, and that of the technical or scientific paper. Abbreviations that might be properly included in the latter, should not be introduced in the former until they have long been used in technical literature. He was especially doubtful as to the advisibility of changing the adjectives to the substantive as a "gooch, a bunsen, a ruhmkorff, or a wiley," and the latter suggests that where one is as fertile as our distinguished associate, there may be a difficulty in determining which one of his many devices shall be called a "wiley."

Dr. Fireman said he did not agree with what had been said as to abstracts. Many papers are not accessible, and possibly only one journal could be obtained. With a good abstract the description of a process may be of use. Neither did he agree with the idea that an historical sketch should be introduced. He thought a summary was frequently of greater use. They are generally brief and give valuable references.

Dr. de Schweinitz closed the discussion by saying that he agreed with Professor Munroe that the style should differ in text-books and in technical papers. What is proper in one is not so in the other. He thought that abbreviations should be dropped as the purpose is to make what is written useful to all, and he thought the ideas and the statements should be expressed as simply and clearly as possible.

A regular meeting was held Thursday, April 9, 1896, with the the President, Dr. E. A. de Schweinitz in the chair, and thirty members and ten guests present.

The minutes of the eighty-seventh meeting were read and approved.

A letter from Dr. Salmon, inclosing a circular letter from the Director of the Pasteur Institute in Paris was read, asking the society to appoint a member to represent it upon the committee to raise funds for the erection of a monument in Paris to Pasteur. The President, Dr. de Schweinitz, was unanimously elected to represent the Chemical Society upon this committee.

There being no further business the reading of papers was proceeded with.

The first paper of the evening was by Mr. V. K. Chestnut upon "Some Vegetable Skin Irritants and their Chemical Composition." The paper consisted of a review of the work of Dunstan and Miss Boole on Croton Oil, and of Pfaff on Toxicodendrol, a new oil-like body from the poison ivy, *Rhus radicans;* together with an account of some vesicating plants which have been but little studied. Specimens of this plant were exhibited and the effect of an alcoholic solution of lead acetate as an antidote to Rhus poisoning was illustrated by experiments carried out by the writer on himself. These experiments also showed conclusively that toxicodendrol was the vesicating principle of the poisonous species of Rhus. Discussion was by Messrs. Tassin, Munroe, Cutter, Stewart, Fireman and de Schweinitz. Mr. Tassin asked whether it was the lead acetate or the alcohol that is the antidote. Mr. Chestnut answered that the alcoholic solution of lead acetate is the best remedial agent. If the oil is kept long enough on persons supposed not to be susceptible, they will be poisoned; the poisoning may take place at the end of twelve hours, or not for five days. Portions of the skin that are thick are not so easily affected as are those where it is thin. Professor Munroe gave his experience as to nitrobenzol, which he had used in considerable quantity, and to which he and the workmen were exposed; it was inhaled as vapor, and came in contact with the skin, but no one was poisoned. The vapor is suffocating, but the workmen soon became accustomed to it. All the books, however, state that it is poisonous. Mr. Cutter said that he could uphold the books, as he had experienced its poisonous effects; he had rigor, fever, chills, and palpitation of the heart, and was unconscious afterwards; the effects lasted for three days, and the smell even now would affect him. Dr. Stewart gave his opinion of its poisonous effects upon the skin; in his own case it had caused an eruption that lasted three or four hours. Dr. Fireman thought that different effects might be produced by vapors and by the liquid; he referred to the effect of hydrofluoric acid vapors, which are not poisonous in any degree, although the liquid was well known to be very poisonous. Professor Munroe thought there might be differences in the substance. Dr. de Schweinitz thought that possibly it was impure in the cases cited by Dr. Cutter and Mr. Stewart.

Mr. Ewell read the second paper of the evening on "The Effect of Acidity on the Development of the Nitrifying Organisms," by E. E. Ewell and H. W. Wiley.

"While it has been known for many years that active nitrification occurs only in the presence of some basic substance capable of neutralizing the free acid as fast as it can be formed, very little time has been devoted to the study of the exact degree of acidity that the nitrifying organisms can endure. As the authors had some forty samples of soil at their disposal during the last year for other purposes, it seemed wise to improve the opportunity to test the influence of acidity on the nitrifying organism contained in the soils from various parts of the country. Tests were made with forty-four different soils, from twenty-two states and territories. The results showed great uniformity in the relation to acidity of the organisms contained in the various soils. Excluding five tests in which no nitrification exists, and five tests in which it was excessive because of the calcareous nature of the soils used for the seeding of the cultures, the average amount of nitrogen nitrified was twenty parts per million; the minimum result of the thirty-four tests included in this average was eleven, and the maximum twenty-five parts per million. The tests are to be repeated with pure cultures of the nitrifying organisms of the same soils. This series of experiments was made as a study of the nitrous organisms only, but the results show that the nitric organisms are not more sentitive to acidity than the nitrous organisms, the final product being nitrate in nearly every case.

Dr. de Schweinitz, referring to the action of acids on the growth of bacteria, said they seemed to be able to accommodate themselves to their environment, especially in the case of the tuberculous bacillus, and after a time they seemed to grow better in an acid medium than in any other, though at first they needed coaxing.

The third paper of the evening was on "The Chemistry of the Cactaceæ," by E. E. Ewell.

Until very recently other species of cacti than *Cereus grandiflorus* and a few related species have generally been regarded as devoid of constituents of pharmacological value. These and other species, have been used in medical practice in the countries in which they grow, but their use has rarely extended to the more civilized nations. Species of the genus *Anhalonium* have long been used for curative and ceremonial purposes by the Indians of Mexico, and the southwestern parts of our own country. They found places in the Mexican pharmacopœia of 1842, under the name of "pellote," or "Peyotl," but have been omitted from the later editions. The dried aerial portions of species *Anhalonium* figure in the commerce of our southwestern border under the name "mescal buttons." The species of this genus have been the subject of scientific investigation by at least three groups of persons during recent years: First, a group of persons at Berlin, where the work was begun by Dr. L. Lewin, the crude material being supplied to him by Messrs. Parke, Davis & Co., of Detroit; second, a group of persons at the Pharmacological Institute at Leipsic, where the work has been conducted by Dr. Arthur Heffter; third, a group of persons in this country, centering in the Bureau of American Ethnology, and including as associates the Division of Chemistry of the United States Department of Agriculture for Chemical studies, Drs. Prentiss and Morgan for a study of physiological properties, and the Botanical Division of the United States Department of Agriculture for the settlement of botanical questions.

Lewin reported the presence of an alkaloid in *Anhalonium lewinii* in 1888. He has given this the name of anhalonin and made an extended report on its physical, chemical and physiological properties in December, 1894. He has also found evidence of physiologically active substances in the related species.

In August, 1894, Heffter reported the presence of a poisonous alkaloid in *A. fissuratum*, to which he gave the name anhalin; he found an extract of *A. prismaticum* to be physiologically active, but did not have sufficient material for a more extended study; he separated an alkaloid that he named pellotin from *A. williamsi*; in *A. lewinii* he found evidence of the presence of three alkaloids, the description of the first of which accords with the description of Lewin's anhalonin. He made an extended study of the chemical, physical and physiological properties of anhalin and pellotin.

In this country, the separation of the constituents of these plants, and the study of the action of the substances thus obtained as well as of the crude materials, upon men and the lower animals, were begun in the autumn of 1894, but before receiving the paper of Heffter. *A. lewinii*, in the form of "mescal buttons," has served as the material for these studies. Anhalonin and a second alkaloid have been separated in considerable quantity. These, as well as other constituents of the drug, including one or more resins, are turned over to Drs. Prentiss and Morgan for physiological experiments, as rapidly as they are obtained in an appropriate state of purity. A complete chemical study of the constituents of the plant is in process, including those substances of interest to the vegetable physiologist as well as those of interest to the therapeutist.

The paper was illustrated with specimens of the cactus of different varieties from the Botanical Gardens and the Department of Agriculture. Mr. Mooney followed with a paper on "The Mescal Ceremony among the Indians."

The mescal plant is a small variety of cactus native to the lower Rio Grande Region, and about the Pecos River in Eastern New Mexico. The botanical name has finally been fixed by Professor Coulter as *Lophophora williamsi*. Mescal is the name by which it is known to the Indian traders, but it is not to be confounded with the other mescal (Maguey) of Arizona. The local Mexican name is *peyote*, a corruption of the original Aztec name, from which it would seem that the plant and ceremony were known as far south as the valley of Mexico, at a period antedating the Spanish conquest. Several closely related species are described by Lumholtz as being used with ceremonial rites among the tribes of the Sierra Madre,

The dry tops, when eaten, produce such marked stimulating and medicinal results and such wonderfully beautiful psychologic effects, without any injurious reaction, that the tribes of the region regard the plant as the vegetable incarnation of the deity, and eat it at regular intervals with solemn religious ceremony of song, prayer and ritual. The ceremonial and medicinal use of the plant was first brought to public notice by James Mooney in a lecture delivered before the Anthropological Society of Washington in 1891, as the result of studies made among the Kiowas and associated tribes of Western Oklahoma. As the ceremony is forbidden, and the trade in the plant made contraband upon the reservations, the investigation was a matter of some difficulty. In 1894 Mr. Mooney brought back a large quantity of the dried mescal, which was turned over to the chemists of the Agricultural Department for analysis, and to Drs. W. P. Prentiss and F. P. Morgan, of Washington, for medical experimentation. The results thus far would seem to indicate that the Indians are right in asserting that they have discovered in the mescal a valuable medicine entirely unknown to science, and which will probably take its place in our pharmacopœia along with those other Indian remedies, quinine and coca. The ceremony and songs are briefly described by Dr. Mooney, whose full investigation of the subject will ultimately appear in one of the publications of the Bureau of American Ethnology.

Dr. Francis P. Morgan followed with a paper on the "Physiological Action and Medicinal Value of Anhalonium lewinii. ("Mescal Buttons.")" Dr. Morgan stated that the investigation had been intrusted to Dr. D. W. Prentiss, with whom he was associated. Experiments were tried and observations taken at regular intervals to determine the action of the entire button on the system. The most striking result was the production of visions of the most remarkable kind with eyes closed, and especially so in the dark. Changes of color were characteristic; tubes of shining light, figures, cubes. balls, faces, landscapes, dances and designs of changing colors were among the most persistent visions. They were hardly seen with the eyes open; in full dose no effect on the reason or will is noticed in most cases. There was direct stimulation of the centers of vision and dilatation of the pupils. About one-quarter of the quantity or three buttons, are sufficient to give the visions in the case of white men. Dr. Morgan detailed the experiences of different persons who had tried the experiments. In some cases there was slowing of the heart, from seventy-five to forty-five beats, followed by a rise to normal; there is also inability to sleep, and a loss of the sense of time—hours seem to intervene between words. The physiological action is not identical with that of any known drug, it is unlike cannabis indica, cocaine, etc. The constituents of the mescal buttons are being experimented with, but the investigations are still incomplete. Anhalonin causes increased reflex irritability and convulsions, like strychnine. It is evidently not the active principle; another constituent has been isolated whose action is widely different. It does not cause opisthotonos, nor tetanus, and has no action like that of strychnine. A third principle has also been isolated. The resin is supposed to be the active principle and will probably be of use in medicine. The experiments are still being conducted and will be detailed later on.

Dr. de Schweinitz expressed the indebtedness of the Society to Mr. Mooney and to Dr. Morgan, and said that the further results would be of interest to the Society.

A regular meeting was held Thursday, May 14, 1896. The president, Dr. de Schweinitz in the chair, with twenty-three members present. Mr. Mayville W. Twitchell was elected as associate member and Mr. Charles N. Forrest as member. The president presented the following resolutions, endorsed by the executive committee, and the Society adopted them; the president and secretary were instructed to sign and transmit them.

WASHINGTON, D. C., May 14, 1896.

TO THE HONORABLE, THE PRESIDENT OF THE UNITED STATES SENATE.

DEAR SIR :—In view of the proposed legislation now before the Senate in the form of a bill entitled "An Act for the further prevention of cruelty to animals in the District of Columbia," which, however, is practically an act to limit, and eventually stop, all experiments upon animals in the District of Columbia, the Chemical Society of Washington, including among its members a number of the most prominent chemists in the country, desires to present to the Senate of the United States a formal and positive protest against the enactment of any legislation upon the subject of vivisection.

The laws at present on the Statute books of the District of Columbia, if properly carried out, will apply to all cases of cruelty to animals which exist in this District. The proposed bill is objectionable for very many reasons. The penalties prescribed for the infraction of the law are preposterous. An expert who did not happen to possess a permit from the District Commissioners for the performance of experiments upon animals might suddenly have placed in his hands material, the dangerous character of which could only be determined by an immediate experiment upon an animal. Should such a test be made without a license, though possibly the lives of hundreds of people were involved, the experimenter would be subject to an enormous fine and imprisonment, for having in the interests of humanity inoculated a guinea pig, or a rabbit, or some other animal, without a formal permit from the District Commissioners.

While the majority of the members of our Society are not directly engaged in experiments in which animals are used, we know that in certain lines of work, toxicology, materia medica, biochemistry, and the like, animal experimentation is absolutely necessary for the advancement of knowledge.

The agitators of the proposed legislation have not been able to show a single instance of cruel experiments conducted in the District of Columbia, either in any of the laboratories, or medical colleges, or public schools, consequently there is no need for any law on the subject. Furthermore, Washington is becoming the center of education for the entire United States. Four large universities are located here; several more are in prospect, and the proposed legislation would hamper and eventually destroy all possibility for advanced postgraduate work in the biological science, and indirectly in all allied branches.

We therefore, collectively as a Society, and individually as members, desire to protest strenuously against any legislation on the subject of vivisection, deeming it to be unwise, unnecessary, and in direct opposition to the spirit which has for a number of years actuated the United States government to encourage the advance of science. We hold further that such legislation would be a direct contradiction of the well-known practical results that have already been obtained by scientific investigations conducted under the government, which have made possible the saving of many thousand dollars worth of property and many human lives.

Yours very respectfully,
[Signed] E. A. de Schweinitz,
Pres. Wash. Chem. Soc.
A. C. Peale,
Secretary.

The president, representing the Society, as a member of the Pasteur Committee, reported that the committee had organized and was ready to receive subscriptions.

There being no further business the reading of papers was proceeded with, Vice President Bigelow taking the chair.

The first paper was by Mr. Frederick P. Dewey, on "Practical Analytical Accuracy."

The paper did not go into the means of securing accuracy, but dealt entirely with the results actually obtained when a number of chemists worked upon the same sample. Not very much has been published in this line, but sufficient has been done to show that the ordinary accuracy of analytical work is not what it ought to be and that there is room for much improvement.

The paper gave results from analytical symposiums published in the Transactions of the American Institute of Mining Engineers and the Proceedings of the Association of Official Agricultural Chemists. It was also somewhat historical in character in tracing the development of accuracy in some determinations.

The discussion of Mr. Dewey's paper was by Messrs. Bigelow and Clarke.

Mr. Bigelow said that Mr. Dewey had selected the most accurate of the determinations by the Official Agricultural Chemists, but Dr. Dewey said he had simply taken those most nearly in his own line of work. He referred to Campbell's tables in the Journal and thought it was unfortunate that nothing was said as to the way they were obtained nor how he was led to adopt the various figures. He allows usually a small variation, but with silica he allows a variation of over one-half per cent, when large quantities are present.

Prof. Clarke thought that a great source of variation between different observers was due to the fact that too great faith was placed in the reagents. The work was not done with the same reagents and reagents are not always the same. Here, therefore, is a source of error.

Mr. Bigelow said he thought another source of error was due to the fact that the work was often done by students or subordinates and these results were published with the others.

Mr. Dewey said his paper was intended to exhibit what was actually obtained every day. He thought the assistant's work was not always the poorest. The principal very often was out of practice.

Dr. P. Fireman read a paper on "A New Mode of Formation of Tertiary and Quarternary Phosphines." When phosphonium iodide is heated with ether in a sealed tube at 160°, for six hours, both ethyl groups of the ether became available for substitution, and these form the hydriodic salts of triethyl- and tetraethylphosphine according to these equations:

$$2PH_4I + 3(C_2H_5)_2O = 2P(C_2H_5)_3.HI + 3H_2O.$$

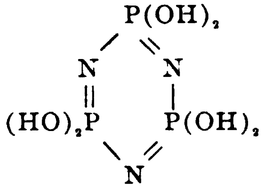
$$2PH_4I + 4(C_2H_5)_2O = 2P(C_2H_5)_4I + 4H_2O.$$

The author is at present occupied with the preparation of the homologous phosphines by the action of PH_4I and homologous ethers. He is also experimenting with a view of obtaining amines by the action of ammonium iodide or ammonium bromide on ethers or alcohols.

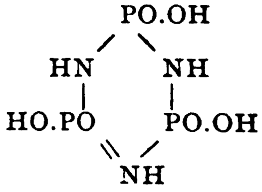
In the discussion of Dr. Fireman's paper Dr. Stokes asked if he had obtained any traces of primary or secondary phosphines. Dr. Fireman answered that primary phosphines are excluded and as to secondary phosphines he had at one time hoped he had obtained them, but he could not say with any certainty that he had. Dr. Stokes thought they might be recognized by the odor. Tertiary phosphines have the odor of hyacinths.

Dr. Stokes then read a paper on "Metaphosphinic Acids."

Dr. H. N. Stokes spoke on his investigation of the metaphosphinic acids, a series of acids having the general formula $(PNO_2H_2)_n$, *i. e.*, metaphosphoric acids in which one-third of the oxygen is replaced by NH. They are not, however, strictly speaking, derivatives of metaphosphoric acids, for while these contain a nucleus consisting of phosphorus atoms united by oxygen, the metaphosphinic acids, as proved by their formation from the chloronitrides $(PNCl_2)_n$, have a nucleus consisting of alternate phosphorus and nitrogen atoms. Two members of the series have been studied, *viz.*, trimetaphosphinic and tetrametaphosphinic acids, $P_3N_3O_6H_6$ and $P_4N_4O_8H_8$, derived from $P_3N_3Cl_6$ and $P_4N_4Cl_8$. Trimetaphosphinic acid apparently has the tautomeric formulas



and



Salts of both forms have been obtained. Under the action of acids, a successive decomposition is effected into $P_3N_2O_8H_7$, $P_2NO_6H_5$, $H_4P_2O_7$, and H_3PO_4. The second of these may be regarded either as $PO(OH)_2.NH.PO(OH)_2$ or $PO(OH)_2.O.$

$PO<^{NH_2}_{OH}$, the former being supported by its derivation from $P_3N_3O_6H_6$, the latter by its easy conversion into pyrophosphoric acid. It presents a peculiar case of intra-molecular wandering of the nitrogen atom, possibly to be explained by a process analogous to Beckmann's transformation. (Particulars will appear in the American Chemical Journal.)

Dr. Fireman said the compounds appeared to him to be of similar constitution as cyanic acid and its derivatives; and also in regard to the tendency to polymerize and to appear in isomeric forms, there is a striking resemblance between both classes of compounds. He thought the results would be of interest in theoretical chemistry. As to the silver salts he asked Dr. Stokes if he had tried to prepare the esters.

Dr. Stokes said that a number of lactams are known that are stable, that open out or have open rings in which the tendency to break up is not marked. The tri acid is easily broken up but the tetra acid is not. In regard to the esters, he had tried to get them from the silver salts, but they are not like the organic ethers. They are very unpleasant to deal with and are coupled mixtures with which little can be done. He had thought of the analogy with cyanic acid and especially with the cyanuric acid compounds. Another theoretical point is the possibility of stereo-isomeric forms. When you have an oxime there are two isomers known. They split up differently — cis and trans bodies. He had not been able to find triphosphinic acid in any but two tautomeric forms.

Prof. Munroe said he was glad to see that the methods of organic chemistry were being applied to inorganic chemistry, but he would like to know why the linear form of the salts was written one way, and read in the reverse way in organic chemistry. He thought it was very confusing to students.

Dr. Stokes thought it was a matter of custom.

Dr. Fireman said he thought that the reason for writing the formula of the organic acid first and then that of the metal was due to the fact that the formulas of the organic acids were usually of a complicated nature and therefore it is natural to dispose of them first and that afterwards it is an easy task to fit in the symbol of the metal.

Prof. Munroe thought this was not the explanation.

Dr. Stokes said different men developed the two methods working from two different sides when a series of homologous compounds is written out. The constants are put down first and then those that vary. This was why he wrote them this way.

Prof. Seaman thought this the correct explanation. Ideas have a different arrangement with different people, normal to each one. He thought there was more uniformity in this country than anywhere else.

The Society adjourned until November.

Issued with July Number, 1896.

Proceedings.

NEW MEMBERS ELECTED JUNE 25, 1896.

Hanna, Prof. Geo. P., Charlotte, N. C.
Harsh, S. A., Revenue Gold Mining & Milling Co., Norris, Mont.
Lederle, Ernest Joseph, Ph.D., Health Department, N. Y. City.
Ludwig, H. T. J., Mount Pleasant, N. C.
McFetridge. Joseph, Natrona, Pa.
Melville, W., Woodmere, Mich.
Mewborne, R. G., Raleigh, N. C.
Miller, H. K., Raleigh, N. C.
Parmelee, Cullen W., 108 Tenth St., Greenpoint, Long Island.
Pegram, W. H., Durham, N. C.
Smalley, Frank W., University of Cincinnati, Cincinnati, O.
Thompson, F., 102 East Seventh St., Covington, Ky.
Uhlig, E. C., care of Whitall, Tatum & Co., 46–48 Barclay St., N. Y. City.
Wood, Joseph R., 240 Green Ave., Brooklyn, N. Y.

ASSOCIATES ELECTED JUNE 25, 1896.

Howell, John W., Edison Lamp Works, Newark, N. J.
Twining, T. E., Newark, Ohio.

CHANGES OF ADDRESS.

Behr, Arno, P. O. Box I, Jersey City.
Eakins, L. G., Box 434, Florence, Colo.
Lane, H. M., care of Great Falls Iron Works, Great Falls, Mont.
Lenher, V., Mechanicsburg, Pa.
Peter, Alfred M., 236 East Maxwell St., Lexington, Ky.
Sargent, Geo. W., Bellwood, Blair Co., Pa.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

The regular meeting of the Section was held Saturday evening, May 16th.

Dr. S. P. Kramer presented "Some New Facts Concerning X Rays," giving an interesting account of some experiments, and exhibiting some negatives made by means of his new five plate Töpler-Holtz machine.

Mr. B. M. Pilhashy, of Cincinnati and Mr. J. N. Hurty, of Indianapolis, were elected members of the Section.

The meeting adjourned until October 15th.

NEBRASKA SECTION.

The Nebraska Section held its fourth regular meeting on June 5th, at 8:00 P. M.

The meeting was called to order by the president. In the absence of the secretary, Mr. J. B. Becher was elected Secretary *pro tem*.

The minutes of the last meeting were read and adopted.

The following officers were elected for the ensuing year: President, H. H. Nicholson; Secretary and Treasurer, Dr. John White; Executive Committee, Samuel Avery, R. S. Hiltner and J. F. Becher.

The Secretary's report was read and approved.

The Treasurer's report having been read, Mr. E. C. Elliott and Miss Rosa Bouton were appointed an auditing committee.

The committee pronounced the report correct, whereupon it was approved.

A letter from J. Stanley Brown, Secretary of the Joint Commission of the Scientific Societies of Washington, was then read, calling attention to the anti-vivisection bill now pending before Congress.

The President appointed a committee to draft suitable resolutions, which were adopted.

"WHEREAS, There is now pending before the Congress of the United States a bill entitled 'A bill for the further prevention of cruelty to animals in the District of Columbia;' and

WHEREAS, In our opinion such legislation is opposed to the proper development of biological and medical science; and

WHEREAS, It is feared that such legislation may be further extended to the several states and territories, thereby very seriously restricting the progress of scientific investigation; be it

Resolved, That the Nebraska Section of the American Chemical Society most earnestly protests against the enactment of such legislation as being unnecessary and prejudicial to the best interests of mankind.

Signed,

H. H. NICHOLSON, President.
ROSA BOUTON,
JOHN WHITE,
EDWARD ELLIOTT,
Committee.

Mr. Benton Dales was elected an associate member.

In the absence of Dr. White, his paper entitled "Contributions to the Chemistry of the Suboxides," was read by Mr. E. E. Nicholson.

NEW YORK SECTION.

The June meeting of the New York Section was held on Friday evening, June 5th, at the College of the City of New York, Prof. A. A. Breneman presiding.

After the reading of the minutes the chairman of the committee on Organization of the Chemical Club reported that at a recent meeting of the committee, held at the Board of Trade, much enthusiasm was shown, and the movement was making good progress.

A communication from the Joint Commission of the Scientific Societies of Washington in regard to the Senate bill 1552, intended to restrict, if not prohibit, vivisection, was taken up and acted upon.

The sentiment of the meeting was unanimous in the direction of preventing affirmative action by Congress on the said bill; and the following resolutions were unanimously adopted, after a full discussion, in which Profs. Sabin, Breneman, Doremus, Hale, and McMurtrie participated.

Resolved, That the New York Section of the American Chemcal Society most earnestly opposes the legislation proposed by Senate bill 1552, entitled "A bill for the further prevention of cruelty to animals in the District of Columbia."

Resolved, That the proposed legislation is unnecessary and would seriously interfere with the advancement of biological science in that district; that it would be especially harmful in its restriction of experiments relating to the cause, prevention, and cure of the infectious diseases of man and of the lower animals; that the researches made in this department of biological and medical science have been of immense benefit to the human race; and that, in general, our knowledge of physiology, of toxicology, and of pathology, forming the basis of scientific medicine, has been largely obtained by experiments upon living animals, and could have been obtained in no other way.

Resolved, That physicians and others who are engaged in research work having for its object the extension of human knowledge and the prevention and cure of disease are the best judges of the character of the experiments required and of the necessity of using anesthetics, and that in our judgment they may be trusted to conduct such experiments in a humane manner, and to give anesthetics when required to prevent pain. To subject them to penalties and to espionage, as is proposed by the bill under consideration, would, we think, be an unjust and unmerited reflection upon a class of men who are entitled to our highest consideration.

Dr. C. A. Doremus read a "Note on the Presence of Oil in Boiler Scale."

Mr. J. A. Matthews described "A New Method of Preparing Phthalimide."

The chair announced this as the last meeting of the season, and stated that the fall and winter meetings would probably be held in the same rooms.

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COUNCIL.

Dr. Drown having resigned from the Committee "to unify the methods of color comparison and report on a standard for measurement of color in potable waters," the President of the American Chemical Society has appointed in his place Mr. Allen Hazen, 85 Water St., Boston, Mass. and Mr. Hazen has accepted the appointment.

CHANGES OF ADDRESS.

Bloomfield, L. M., Ohio Experiment Station, Wooster, Ohio.
Booraem, J. V. V., Box 190, Glen Cove, N. Y.
Fuller, Fred. D., Durham, N. H.
Lippincott, Warren B., North Western Iron Co., Mayville, Wis.
Mar, F. W., 138 First Ave., West Haven, Conn.
Myers, H. Ely, Carnegie Steel Co. Ltd., Lucy Furnace, Pittsburg, Pa.

MEETINGS OF THE SECTIONS.

NORTH CAROLINA SECTION.

The summer meeting was called to order at 3.30 P. M., July 7th, in the Chemical Lecture Room of the University of North Carolina. There were ten members in attendance. The secretary reported ten new applicants for membership, who were duly elected. There were other applicants who had not yet conformed to the condition of becoming members of the American Chemical Society. The membership roll has doubled in less than a half-year.

Resolutions were offered and adopted with regard to the vivisection bill and the appointment of a director-in-chief of the Scientific Bureaus of the Department of Agriculture. The following papers were then read:

"Crystallized Aluminum," by F. P. Venable; "Detection and Purification of Saccharin," by B. W. Kilgore; "Reduction of Sulphuric Acid," by Chas. Baskerville; "Comparison of Digestibility of Raw and Steamed Cotton Seed," by J. A. Bizzell; "An Attempt to Form some Organic Compounds of Zirconium," by Thomas Clarke; "Determination of Sulphur in the Presence of Iron," by W. A. Withers and R. G. Mewborne; "Action of Phosphorus Trichloride on an Ethereal Solution of Hydrogen Dioxide," by W. A. Withers and G. S. Fraps; "Some Difficulties in the Way of the Periodic Law," by F. P. Venable.

The section then adjourned.

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CHANGES OF ADDRESS.

Beeson, J. L., Bethel College, Russellville, Ky.
Best, Dr. Otto, care of Fritzche Bros., Garfield, N. J.
Haines, Reuben, Haines and Chew streets, Germantown, Pa.
Emmens, Stephen H., 179 Washington Building, N. Y. City.
Kelley, J. H., Bentonville, Ark.
Moale, Philip R., 82 Chestnut street, Asheville, N. C.
Mumper, W. N., 823 W. State street, Trenton, N. J.
Nichols, Wm. H., 32 Liberty street, N. Y. City.
Potter, Wm. R., 100 Broad street, Providence, R. I.

DECEASED.

Bower, Henry, Gray's Ferry Road, Philadelphia, Pa.

MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

The regular monthly meeting of the Rhode Island Section was held at Providence, May 21, 1896, Mr. Charles S. Bush in the chair.

A paper was presented by Mr. William R. Potter, upon "Fallacies in Urine Analysis due to the Presence of Salicylic Acid and its Compounds."

After a brief introduction of the value of urine examination as an aid to the physician in his diagnosis, the reader described in detail the influence salicylic acid had upon the albumin test and the glucose test as commonly practiced. The chief source of error was pointed out to lie in the sparing solubility of salicylic acid in an aqueous solution, and the ease with which its compounds were decomposed by other acids.

The annual meeting of the Rhode Island Section was held at Pawtucket, R. I., on Thursday afternoon, June 11, 1896.

Members met upon the invitation of the presiding officer, Mr. C. A. Catlin, at the Country Club. After dinner the annual election of officers took place. The following were elected for the ensuing year:

Presiding Officer, Mr. Edward D. Pearce ; Secretary and

Treasurer, Mr. Walter M. Saunders; Member of the Executive Committee, Mr. George F. Andrews.

The retiring chairman then presented his annual address, taking for his topic, the subject of chemically-applied mechanics, introducing it by brief historical reference to the progress of chemistry, more particularly to the development of apparatus and improvements along the line of chemical manipulation. It appears that after all the same forms of retort and crucible that did service in the time of Zosimus, are still the stereotyped forms of the chemical supply house.

Great progress in recent years in arts dependent upon chemistry, has, however forced the development of apparatus, and the application of mechanical expedients, until there has grown up what may in all truth be called the science of chemically-applied mechanics, practically unrecognized as yet by the training schools of the profession, though covered in a general way by courses offered in chemical engineering. These courses do not meet the case. The real demand is, that chemical students shall have opportunity in training, to pursue the study of practical mechanics as applied to chemical manipulation, simply a new study added to the old curriculum. Illustrating something of the scope of this chemically-applied mechanics, may be cited, hydraulics, for instance, as applied to the handling of liquids, the speaker showing from his own practical experience how the attendant phenomena of the various filtering methods, may, by a general classification, be brought to useful presentation of the whole subject. Further may be cited pneumatics as applied to the manipulation of air draughts, the charging of liquids with gases, etc., strength and adaptability of materials to the construction of apparatus, their acid or alkaline resisting qualities, with effects of saline solutions upon them; heat in its varied application; light in the practical application of its actinic properties; and the milling of materials. Again illustrating particularly, the speaker showed how the attendant phenomena of the various milling processes may be brought under general statements for better consideration.

Generally the scope of chemically-applied mechanics may be stated as the application of mechanical principles to chemical manipulations. The whole subject should be presented to the chemical student in a general way, setting forth at least the fundamentals along these and related lines, expanding into particular detail in the more important, thus broadly laying the foundation for the development and exercise of the inventive faculty in applying mechanical means to special chemical requirements, whether it be in the factory or the research laboratory.

Issued with October Number, 1896.

Proceedings.

THIRTEENTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

BUFFALO, N. Y., August 21, 1896.

President Dr. Charles B. Dudley called the meeting to order. Dr. Roswell Park, President of the Buffalo Society of Natural Sciences, welcomed the visiting chemists as follows:

Mr. President and Gentlemen of the Chemical Society: I am very glad to join with my friends in the City of Buffalo in welcoming you here. My idea of what should be said on such an occasion, is that it should be characterized by genuineness rather than eloquence, by brevity rather than length. I am sure we are very glad to see you here. I know that this is the first time the Chemical Society ever met in Buffalo, and we hope that you will like us so well that you will come again. I have on several occasions in time past welcomed associations of citizens here. I tell them we have pleasant weather here always. I was sure in my own mind that you would have it. It is a promise we can safely make anytime in the summer. Buffalo seems to be generally regarded now as the ideal convention city. We have had a convention here of some kind almost every week, and this will continue through September. There are meetings here almost all the time. If you study our statistics you will find us the healthiest city in the country. If you will travel around our streets you will discover we have the most attractive residential city in the country. And in every way, both from our treatment of you and what you see for yourselves, we hope you will feel thoroughly welcome, and thoroughly at home.

It is always proper, I think, on such occasions, to blow our own horn a little bit. I have found so little appreciation of Buffalo abroad, of what Buffalo is, that I am going to say a little to you about Buffalo. It is the sixth commercial city in the world. That is not generally appreciated. A friend of mine went to Boston and while there was talking to a friend of his in that city about Buffalo. The Boston man said, "Buffalo? Is that on Lake Erie or Lake Ontario?" At the same time, we have a much greater tonnage coming into our harbor in one year than comes into Boston harbor. That he overlooked. About 5,000,000 tons of tonnage enter our harbor, and about the same leave our harbor every year. There is only one other city can say this, and that is Liverpool. That is not generally appreciated. Thirteen years ago, when I moved here, the city had about 125,000 inhabitants; now it has a third of a million, so you can get an idea of how it is growing. We who live here and see the trend of affairs, look forward to a time when there will be but one city to Niagara Falls. We are coming nearer and nearer to that all the time. It is not far off, I assure you.

Now, with all we have and all we can do for you, gentlemen, you certainly are cordially welcome. You will hear more of this, as I expect you will attend the meetings next week, and perhaps be more formally welcomed by the city officials on other occasions; but our homes are opened to you, and everything we can do in any way for you, is cordially placed before you.

To refer just a moment to the scientific aspect of this gathering, I have never had a chance to talk to professional chemists before, and there is one appeal I want to make to you as coming from our profession to yours. Of course we are working in large measure on common ground; especially when it comes to physiological chemistry, and in the chemistry of the fluids, etc., of the body, we are on absolutely common ground; but there is very much we have to rely upon you for, in order to help ourselves forward; and, as one who is eagerly anxious for the discovery of a particular substance, an ideal in our business, which you only can probably furnish, I will make this scientific appeal to you. We have been working for years to find a substance which shall have a germicidal property so far as deleterious agents are concerned, and yet which will not be toxic with the tissues of the human body; a chemical substance whose relative and absolute toxicity are far enough apart to make it a safe substance to use. When we have that, we hope to saturate the human body with the substance which will be at the same time not toxic with the tissues of the larger organs. I do not know whether that time will ever come. It seems to me an ideal substance. I do not know how you, who are so interested in the affairs of the world at large, as well as humanitarians, can make a better discovery than one along the lines I have suggested. It is not for commercial purposes, but purely for the benefit of humanity. You will pardon this little appeal to your chemical abilities; it is the only chance I have ever had to make it.

Permit me only to reiterate what I have said to you about the cordiality of our welcome, our earnest endeavor to extend to you our hospitality, our earnest hope that your first meeting will not only be so successful that you will look back to it hereafter, but will be so pleasant to you that you will want to come here again quite often. (Applause.)

The President.

Dr. Park, The Committee of Arrangements, and Fellow Members of the American Chemical Society: I am sure I voice the sentiment of those who are present when I say that we appreciate this kind welcome, and we thank you for it. I doubt not there are a good many present who can well remember when chemical analysis, except for purely scientific purposes, was a rarity. In my early student days the chemical analyses that were made, except as I say, for such purely scientific purposes, were largely made by the professors in colleges. They were slow. They were very expensive and any business that wanted a chemical analysis, studied quite a while before employing a chemist to make it. That state of affairs is now changed. With the growth of the technical school there has come forward each year a large crop of young, enthusiastic chemists, and with this supply, if I may use the word, has come likewise the necessity for their existence and the work for them. I am not saying anything more than is known to you all when I say that a very large number of commercial ventures and enterprises to-day cannot live without their chemist. The steel works would not be able to maintain themselves a month without a chemist. The sugar industry needs the chemist, the brewing industry, the textile industry, and, indeed, I might go on and enumerate occupation after occupation which is based largely upon the chemist's work. The railroads, as you know, are using chemists, and the cities begin to have their chemists to protect people against fraud and adulteration in products which are for sale. As we all know, agriculture is more and more every day becoming based on chemistry, and our government itself supports one of the best chemical establishments in the world.

Now, this increase in chemists, this increase in their work, this demand for them, has led to another necessity; namely, that the chemists should occasionally look each other in the face, that they should talk things over with each other, that they should profit by each other's work, and that brings us to state what the organization of the Chemical Society is, an organization with something like 1,000 members, an organization which supports a Journal that is published every month, and with some eight or nine local sections located in different parts of the country. This organization must, as we all know, have a place for meetings. We are already having two meetings every year and this year we come to Buffalo, and I may say, that this city is the Mecca to which all scientific men are travelling this year—this city which may almost be called the mother of scientific organizations. I believe that the reorganization of the American Association for the Advancement of Science, one of the oldest scientific organizations in the country as we all know, took place here in Buffalo in 1866, after the war. It had previously had existence but the war injured it, or caused a temporary cessation and the reorganization took place in Buffalo. Thus much for our reason for existence and thus much for our coming here. We appreciate very greatly your kind and gracious welcome. We look forward to an interesting and profitable time. We thank you. (Applause.)

The following papers were then read and discussed :

"Mercuric Chlorothiocyanate," by Charles H. Herty and J. G. Smith. Read by Dr. Herty. Discussed by Messrs. Hart, Prescott and Frankforter.

"The Reduction of Concentrated Sulphuric Acid by Copper," by Charles Baskerville. Read by the author.

"Notes on the Preparation of Glucinum," by Edward Hart. (An informal description of the progress of work on the preparation of glucinum and its alloys. A glucina crucible was exhibited and also some nearly pure glucina prepared by the method already described in the Journal, **17**, 604. This glucina apparently contains the same unknown substance already detected by Kruss, and as 200 pounds of beryl are being operated on it is hoped that enough may be obtained for its identification.) The paper was discussed by Messrs C. B. Dudley and Hart.

"The Inspection and Sanitary Analysis of Ice," by C. L. Kennicott. Read by the author. Discussed by Messrs. W. P. Mason, Cochran, McKenna, W. A. Noyes, Breneman, Miller, Phillips, Robbins, Frankforter and C. B. Dudley.

"A New Form of Potash Bulb," by M. Gomberg. Read by Dr. Prescott. Discussed by Mr. Phillips.

"Morphine in Putrefactive Tissue," by H. T. Smith. Read by Dr. Prescott. Discussed by Mr. Miller.

"Some New Compounds of Thallium," by L. M. Dennis and Martha Doan, with crystallographic notes by A. C. Gill. Read by Dr. Dennis. Discussed by Messrs. Prescott, Hart, Frankforter and Mason.

The President: It has reached pretty nearly the hour of adjournment and I would like to make an announcement or two as to the work of the Society during the interim. Early in the spring a letter was received by the Society stating that Cannizzaro's seventieth birthday was to occur on the 11th of July, and it was proposed to make a testimonial to him in some way. This letter asked the cooperation of the American Chemical Society. After talking the matter over it was decided since Cannizzaro was already an honorary member that we should send him a testimonial engrossed on parchment. This was duly prepared and was sent in time to reach Rome some two or three weeks before his birthday. However, since that time we have received a second letter stating that owing to the fact that most of the professional people who were interested in Cannizzaro were out of town during the very warm season, it has been decided to postpone the public recognition of the occasion until later in the fall, I think some time in October. So we have not as yet heard from the other side as to what has been done with the testimonial. I would say likewise that in this letter there was a statement to the effect that the form, which recognition was taking on the other side was that of accumulating a fund to be used for some scientific purpose.

I would also state that at the last meeting of the Society in Cleveland a committee of three was appointed to take up the question of coal analysis. That committee consisted of Mr. Hillebrand of the Coast Survey, Chairman, Prof. W. A. Noyes and the President of the Society. The committee has been able to do very little thus far except to get ready. They are not prepared to make any formal report at this meeting, partly, I think due to my own fault in the matter. Our progress has not been sufficient to make a formal report. This is simply to let you know that the subject has not been dropped.

About the beginning of the summer a paper was read in the New York Section by Prof. Leeds on the color of water, and at his suggestion a Committee was appointed to report to the Society, a standard to be used for determining the color of water and a method. That committee consists of Prof. Leeds, Chairman, Prof. Mason and Mr. Allen Hazen, formerly connected with the State Board of Health of Massachusetts, who has done a good deal of work on water analysis. We have some regular or standing committees; I have not been able to get in communication with the Chairmen of all of them as yet, and we will try to-morrow to see whether we can get information from them on the state of the subjects committed to them. After some announcements by the general secretary and the local committee of arrangements, the session adjourned.

SATURDAY MORNING, AUGUST 22, 1896.

The President called the Convention to order at 9:40 o'clock.

The President: As we have considerable to get through with to-day I think we had better start as soon as possible and first of all I will ask the Society to give two or three minutes to Dr. de Schweinitz who wants to present the matter of the Pasteur monument.

Dr. de Schweinitz: Mr. President and gentlemen of the

Society: I only desire to detain you for a moment to ask for subscriptions towards the erection of an international monument in Paris to Pasteur. The French Government has organized this movement and requested the cooperation of all scientists, or I should say, rather, of all members of the different branches of science in the United States. As Pasteur was a chemist, the chemists of the United States should be the first to respond to this request. Printed blanks of a general announcement, giving the names of the members of the French committee, and also of the organizing committee of Washington, which has been started, will be distributed, and in addition to this subscription blanks, as you see here, upon which you are requested to place the amount, however small, it does not make any difference, and however large, the larger the better and the more will the contribution be appreciated, to be forwarded to Washington. These blanks with the names and the amounts will be preserved and will be deposited in Paris in the archives in connection with this Pasteur monument. I will distribute these blanks and be greatly obliged to the members of this Society if they will join in the contribution at as early a date as possible and to the largest amount that they feel able to give.

The President: I am sure the appeal is one that we are all interested in, and if chemists can see their way to subscribe for this purpose, we shall be very glad. We all feel willing undoubtedly, but possibly not all of us are able.

Dr. de Schweinitz: Mr. President, I might add that the subscriptions so far received have varied in amount from twenty-five cents up, so that no one need have any hesitancy on that subject.

The President: I presume there is no one can not subscribe at least the minimum amount.

I wish to say that Dr. Levi has brought up a few samples of aniline colors made at the aniline works, which there was no opportunity to distribute yesterday, and anyone here can avail himself of the samples if he so desires.

The following papers were then read and discussed:

"Contribution to the Knowledge of Rutheno Cyanides," by James Lewis Howe. Read by the author.

"Analytical Methods Involving the Use of Hydrogen Dioxide," by B. B. Ross. Read by the author.

Prof. Hart: Mr. Chairman, while we are waiting for Prof. Ross to place these figures on the blackboard, there is a matter that has been called to my attention which I would like to present to you; it will only take a half minute; this is connected with the subject of advertising for the Journal. By resolution of the Board of Directors I was appointed a committee of one to secure advertisements for the Journal. This is an important source of revenue, and we have derived considerable money to be applied to the publication of the Journal in this way. It is believed that with some additional assistance this source of revenue can be still further increased. We have to depend for this assistance on voluntary aid, and I wish to acknowledge the great assistance I have already received from Dr. McMurtrie in this direction. The Society is indebted to him more than is perhaps generally known. It has been suggested to me that a number of members of the Society would be willing to assist in the matter of procuring advertisements, and that it would be well to increase the committee to ten members. These members would then feel that it was their duty to assist in securing the advertisements, and it is believed that this will result in securing considerable additional patronage. I therefore move that the President have power to increase the committee to not more than ten members.

Dr. Hale: I second the motion.

Dr. McMurtrie: I think it might be well further to give the committee power to extend its membership in case that appears desirable. I would move to amend in that manner.

Prof. Hart: I accept the amendment.

President Dudley put the motion as amended, and it was duly carried.

The following papers were then read:

"The Estimation of Thoria; Chemical Analysis of Monazite Sand," by Charles Glaser. Read by Dr. Hart.

"The Estimation of Thorium and its Separation from Other Rare Earths," by L. M. Dennis. Read by the author. These two papers were discussed by F. W. Clarke and L. M. Dennis.

"A Complete Analysis of Phytolacca Decandra," by G. B. Frankforter and Francis Ramaley Read by Mr. Frankforter.

"The Crystallized Salts of Phytolacca Decandra," by G. B. Frankforter and Francis Ramaley. Read by Mr. Frankforter. Discussed by A. B. Prescott.

"The By-Products formed in the Conversion of Narcoline into Narceine," by G. B. Frankforter. Read by the author.

"The Composition of American Kaolins," by C. F. Mabery and Otis T. Klooz. Read by Dr. Hart. Discussed by Messrs. Dudley, Baskerville, McMurtrie, Noyes, Prochazka, Breneman and Patrick.

The following papers were read by title:

"Composition of Certain Mineral Waters in Northwestern Pennsylvania," by A. E. Robinson and Charles F. Mabery.

"Zirconium Oxalates," by F. P. Venable and Charles Baskerville.

"Aluminum Analysis," by James Otis Handy.

"An Analytical Investigation of the Hydrolysis of Starch by Acids," by George W. Rolfe and George Defren.

"The Effect of an Excess of Reagent in the Precipitation of Barium Sulphate," by C. W. Foulk. Discussion by T. M. Gladding.

"Determination of Reducing Sugars in Terms of Cupric Oxide," by George Defren.

"Acidity of Milk Increased by Boracic Acid," by E. H. Farrington.

"The Actual Accuracy of Chemical Analysis," by Frederic P. Dewey.

"Some Extensions of the Plaster of Paris Method in Blowpipe Analysis," by W. W. Andrews.

"Device for Rapidly Measuring and Discharging a Definite Amount of Liquid," by Edward L. Smith.

"Table of Factors," by E. H. Miller.

"A Modified Form of the Ebullioscope," by H. W. Wiley.

"The Signification of Soil Analysis," by H. W. Wiley.

"Notes on the Determination of Phosphorus in Steel and Cast Iron," by George Auchy.

"The Development of Smokeless Powder," by C. E. Munroe.

The President: I would like to announce that the winter meeting will be held in Troy, it having been decided by the Council, on the invitation of our membership in Troy to hold the meeting at that place. We are hoping to make that meeting one of the best the Society has ever had and I would like to ask Prof. Mason to give us a word or two in regard to our meeting next winter at Troy.

Prof. Mason: Mr. President and fellow members, it has been very gratifying to me to learn that you have decided to come to Troy. We are not a large city, but we will do our very best to make your stay agreeable. There are some things there that are worth seeing. We will be able to show you the largest gun plant in the world, much larger than Krupp's. Of course when you speak about Krupp's plant it means his whole concern, the gun plant and that for other varieties of iron and steel manufacture as well, but the gun portion of his plant would go into a small part of the United States gun plant which you will see at Troy. As you know, all the artillery now used by the army is made there, practically; I believe there are a few unfinished contracts out, but I am not positive about that. You will be able to see electric cranes that I think are larger than you have ever seen elsewhere. You will be able to see guns in all stages of manufacture. I hope you will be able to see an old-fashioned smooth bore of fifteen or twenty inches caliber lying along side of a modern twelve or thirteen. It looks like a soda water bottle. We have some other institutions there that we are proud of, for instance the new basic steel plant, which will be in full operation by the time you get there, the Burden Iron Works where they make Burden's best iron, which you have often heard of. The shirt foundries and collar smelting works with their attendants are well worth seeing. (Laughter.) More particularly the E & W Collar. You have probably heard of them. They have sent you a special invitation. We have N + 1 breweries in Troy. We can take care of the N and we have assigned the 1 to our President. (Laughter.)

It will give us great pleasure to see you and I am heartily glad that you are coming and the Mayor of the city sends his especial invitation.

The President: I am sure we will all look forward to this meeting with a great deal of interest, and as I said at the very outset we hope to make this the most important meeting the Society has ever had. At this point and *a propos* here I want to give you a word of exhortation in regard to the condition of the society. As everybody knows the most important thing in the Society is the Journal. The Journal is impossible without money. Our rates are low, our annual dues being only $5.00. The Society of Civil Engineers in this country charges $15.00, the Mechanical Engineers $15.00, the Mining Engineers $10.00, the Mining Institute of Great Britain two guineas; the German Mining and Steel Institute charges $10.00. We are trying to run a Society on $5.00 and the management does not think at present that it would be advisable to raise that figure. But we want more money. How can we get more money? Obviously by getting more members. If every member of the Society would get one, think what would happen the doubling of our membership. It is believed there are something like 5,000 chemists in the United States who are eligible, either as full members or associates. We have practically now about 1,000. Your management has in mind plans in regard to the advancement of the Journal to make it still more representative, having it cover wider fields, but for this purpose money is necessary, and money with our present ideas in regard to our present society can only come to us, at least as far as we can see, through increase in membership. Will not every member of the society do something in the next four or five months to increase our membership. We certainly are well established on a good foundation. It is an honor to be a member of our society. We give a full requital for everything we get from our membership, and certainly the time is fast approaching when any American chemist who expects to keep up with his profession cannot afford to be outside of the Society. Let every member bring one member with him and more if possible, at the Troy meeting or bring them in between now and then. I will call upon the Secretary for a few announcements connected with the Society.

The Secretary : Perhaps I might say, Mr. President, that Dr. Mason with becoming modesty has failed to remind you that the oldest institution, if I am not mistaken, for the education of civil engineers, is in Troy, and as a representative of the institution, he has some modesty in speaking of it. Allow me to call attention to one point in reference to increase in membership; there is provided in the constitution a class of members who are not necessarily chemists, but who are interested in chemistry, the associates; and it would seem as though there might be a large amount of recruiting from this source. There are very many people who do not feel themselves distinctively chemists and yet they are interested either through their business or by their inclination in the development of chemistry; and it would seem possible to have as large a membership of associates as of active members. We can do a good work in that way, and the $5.00 of an associate is worth just as much as the $5.00 of an active member.

In regard to the membership of the society, I would say that last spring, somewhere about March, I think, for the first time in the history of the Society, we struck a membership of a full round 1000 in number. (Applause.)

The President: I am sure those of us who have the pleasure of being at this meeting can not fail to have recognized that there has been at the helm some guiding hands, and I am going to say for your information that those guiding hands are not the officers of the Society but the local committee. I feel that it would be improper for us to close the meeting without some recognition of the kindness we have received at the hands of our members here and also those who have contributed to our happiness during this visit. I will call upon Prof. Mason to propose due recognition.

Prof. Mason: Mr. President and Gentlemen; it seems to me entirely fitting that we should pass a vote of thanks to those who have so kindly looked after our pleasure and interest, and I will therefore move you that the thanks of this society are due to the local committee of arrangements, Drs. H. M. Hill, J. A. Miller, T. B. Carpenter, L. E. Levi, also to the local committee of the American Association for the Advancement of Science, especially Mr. Eben P. Dorr, Secretary, also to the local press and to the managers and directors of the various works visited; namely, the Milsom Rendering and Fertilizing Works, Garbage Reduction

Works, Lang's Brewery, Buffalo Reduction Company, Calcium Carbide Works (Niagara Works), Cataract Construction Company, Cliff Paper Mill, Tonawanda Iron and Steel Company, Schoellkopf Aniline and Chemical Company, Crystal Water Company, also Jaeger's Roof Garden and Café.

The President put the question on the adoption of the motion, which was carried unanimously.

The President: Is there any further information desired or any further question to come up?

Prof. Mason: May I ask this question: Is it possible to so arrange matters as to consolidate the summer meetings of the Chemical Society and Section C? I ask it because I personally can be away but a week. The two meetings occupy more than a week. I should like to attend the two meetings in full, but I can not do it. My position is such that I am obliged to return next Wednesday night. The result is I cut off half nearly of the American Association meeting. Inasmuch as it is a meeting of almost the same men under different names, is it not possible to so arrange matters as to have them all together.

Dr. Norton: I feel very much as Dr. Mason does. In order to bring this to decisive action I move you that the Council be authorized to use its discretion in arranging for a joint meeting of this society and Section C of the American Association next year. I think this will enable us to give an expression to our feelings and leave the Council free to take the proper measures. I know a number of our members are coming on next week. They do not feel as though they could give nine or ten days to the meeting of both societies. There are a number present in the room who will have to leave next Monday or Tuesday. By a little careful study we can arrange to have the whole chemical work that would come before the Society and before Section C of the American Association, carried on in the sessions of the five days which are given up for that purpose. I think it would be much more desirable because we do not want our membership stringing along through some seven days, part of us listening to papers now, and part at the end of the week. I feel from conversation with a number of our members that there is a general belief that we ought to have some simple arrangement for joint meetings, and they can be presided over alternately by the President of our Society and the vice-president of Section C.

Mr. Prescott: I second the motion, and I think at the present time when the meetings of the Association are as they are, that the plan can be carried out much better than it would have been before the present arrangement had taken place.

Prof. Hart: I second the motion, Mr. President, but I wish to point out one matter that ought to be thought of, that is, the increasing number of papers. We have ten more papers at this meeting than we had last year, and most of you have already received programs of Section C of the American Association and can see what an enormous program that is. People who take the trouble and pains to prepare papers for these meetings naturally feel that they would like to have the papers read. That is a thing to which we should give careful recognition. If anything of the kind is done it is not possible, I think, to secure any more time in Section C than we have now, and according to the printed program that time is already taken up. We have not read more than one-half the papers.

Prof. Kennicott: It does not seem to me it would be a wise thing to sink our identity in any other society. Simply to meet with Section C would seem to me to be loss of identity.

Dr. Hale: Mr. President, it seems to me the motion that has been made is eminently a proper one. The various points one way or the other of difficulty or ease of adjustment would come properly before the Council for consideration and they would have plenty of time to confer with one another and consider the subject. Certain it is that we have a large number of chemists who are increasingly loyal and devoted both to the American Chemical Society and Section C, and by bringing the chemists together at this time we have undoubtedly added to the attendance and the interest and the number of papers of both. It seems to me that the whole subject is wisely referred to the Council of the Society, and of course Section C can take whatever similar action it chooses.

Mr. Breneman: I am quite in accord with the resolution, but it seems to me it would simplify matters very much if we should simply decide to abolish the summer meeting and let the winter meeting be the only one. That is the annual meeting; it is the meeting where the election occurs and the one of greatest interest. I do not see any reason for a joint meeting. If the arrangement suggested is made, the winter meeting will be distinctive and the only annual meeting of the society.

Prof. Kennicott: I see that my predictions are to be verified. We have already started to sink the identity of the Society. A great many members would be unable to attend any meeting in the winter.

Dr. Prescott: Mr. President, I think the Council would be very glad if we could have a general expression of opinion like that of Prof. Kennicott and others very briefly at this time.

Dr. Howe: The suggestion that has been made is one I remember when the original discussion took place in regard to the reorganization of the Chemical Society. It was proposed at that time that the American Chemical Society should have its winter meeting, but that the summer meeting should not be for the reading of papers; that the papers then should be read at the meeting of the American Association. It certainly is not desirable to carry on any merging of identity, at the same time it seems to me that the plan suggested would be a valuable one to those of us who are present here as chemists, and more valuable than the present plan, if we can mass together all the papers and have all the members present in a four days' session, so that we could have the fullest and most helpful discussion. Some of us are unfortunately unable to be present at the winter meeting, but I think even for us it would be better if all the papers were presented together in the meeting of the American Association in the summer. It does not seem to me we want to do anything to injure the American Association or have things in such a situation that we feel obliged to come here this week and go off next week and miss everything that goes on in the Association. I think the Association owes a great deal to the Chemical Society for what it has done in stirring up an interest again in Section C. I think there should be some amicable arrangement of this matter.

Prof. Mason: Just one word I would like to say. We come here, it is true, to listen to chemical papers, but we also come to meet chemists, and if we have an opportunity of meeting all the members of the American Chemical Society and the members of Section C as well, we fulfil the second object we came for better than if we should string the meeting over so many days, and as a result one man goes before another arrives and perhaps they want to see each other.

Dr. McMurtrie: Mr. Chairman, there are some difficulties that occur to me in this connection. The matter has been of course discussed a good deal during the past three or four or five years; it had been when the reorganization of the Chemical Society occurred, and one of the important difficulties has arisen to my mind during the last year or so when I have been more or less active in the work of Section C of the American Association. In preparing the program of proceedings for last year I was reminded that it was impossible to have papers presented in the meetings of Section C by any other than members of the American Association. Now there is a larger portion of the membership of the American Chemical Society who are not members of Section C. The consolidation of the meetings will necessarily rule out those men from participation in the meeting. This point would of course be brought before the Council in a discussion of the matter, and would, I suppose, have weight. There are a good many members of the Chemical Society, I know, who feel that they do not care to have membership in the American Association, and it seems to me that in any action we take in this regard their wishes should be carefully considered. I think it might be possible to arrange to have the meetings succeed each other in the same week, but that arrangement which has been followed in the past year, has been objected to by the officers of the American Association, holding that it interfered in a large measure with the work of the Association. It was in a measure on this account that the meetings of the Association are fixed for the week continuously; that is beginning with Monday. So that those societies which are called by the officers of the Association, affiliated societies might have their meeting either in the week preceding or succeeding the meeting of the Association. There seems to be a feeling, I think, among a good many of the officers of the Association that it would be in a measure impossible to secure the coalescence of the different societies with the similar sections. As I say, all these points will be brought necessarily before the Council in the discussion of the matter, and it is the only way in which it can be determined after all. It must, under the constitution, go before the Council before it is open again to be brought before the Society.

Mr. Cochran : Before the question is put I would like to ask one question, and that is this : I myself see some objections to it, but I do want to attain it; I would like to attend both meetings if I could; I would like to be here when all the chemists are here. This year particularly, my time is very limited ; I shall leave Buffalo this evening and be cut out of the meetings next week entirely. The question I wanted to ask is this: Is it impossible that both meetings should run on at the same time? Could we not have a section meeting or the meeting of the American Chemical Society conducted at the same time that the meeting of Section C of the American Association is conducted? The programs are large. Some of us would desire to hear papers in one section one week and some in the other, and in that way we could save our time and get the papers presented so that we could all hear them. I know there are objections to it, but at the same time I desire to have the subject considered.

Dr. McMurtrie : We are not alone in this matter. Nearly all the other sections of the Association are in about the same position, and it is coming to be a serious question as to what shall be done in this matter, whether the American Association shall be taken into a confederation of scientific societies, or whether some such plan as is suggested now shall be carried out. It seems to me that this might be permitted to grow into a confederation.

The President: I was about to remark on that same subject that there are other affiliated bodies exactly in the same position as Dr. McMurtrie has said, so that it is obvious this question is a serious one.

The President put the question and it was adopted.

Dr. Norton: Mr. President, I would like to say a few words as to what has been said in regard to the pleasure and profit we have all had in meeting together as a Society during the past few days, and I feel that our success, which is actually a marked one this year in point of attendance and interest, is due not only to the efforts of our Local Committee, but also to the able preparation made in advance for the meeting by the officers of the Society, and I would therefore like to move before we separate to-day, that the cordial thanks of the Society be expressed to the President and Secretary for the measures which they have taken to render this meeting so successful, and I would like to ask the Nestor of the Society, Dr. Prescott, to put that motion.

Dr. Prescott: I am very glad to place this motion before you and have an opportunity to vote for it.

Dr. Prescott put the motion which was unanimously carried.

The President: In behalf of the officers, I will only say that it is a regret on their part that most of us are so busy with our daily life that we can not give all that is in our hearts and minds to do for the interests of the Society, and we thank you for your vote. (Applause).

The President: I declare then the meeting adjourned until the Troy meeting.

ANNOUNCEMENT.

All persons who have papers to offer for the next general meeting, which will be held the latter part of December in Troy, N. Y., are requested to forward at their *earliest opportunity* an abstract, or the full manuscript of their papers together with titles and names of authors to the General Secretary, Albert C. Hale, 551 Putnam Ave., Brooklyn, N. Y., so that the papers may all be passed upon by the committee on papers and publications in time for announcement upon the program which must be in print before the meeting.

CHANGES OF ADDRESS.

Burt, M. C., 106 Chestnut St., Springfield, Mass.

Conradson, P. H., Franklin, Pa.

Eakins, L. G., care of Guppenheim Smelting Co., Perth Amboy, N. J.

Lane, Henry M., care of Washington Agricultural College, Pullman, Wash.

Mar, F. W., 32 McDonough St., Brooklyn, N. Y.

McCrae, John, 7 Kirklee Gardens, Kelvinside, Glasgow, Scotland.

Welles, Albert H., 635 Quincy Ave., Scranton, Pa.

Whitehead, Robt. L., Box 142, Mt. Washington, Md.

Issued with November Number, 1896.

Proceedings.

COUNCIL.

By direction of the Council a congratulatory address was forwarded to Stanislas Canizzaro, an honorary member of this Society, upon his seventieth birthday.

December 29 and 30 has been selected as the date for the annual meeting at Troy, N. Y.

MEMBERS ELECTED SEPTEMBER 21, 1896.

Belden, A. W., Chapel Hill, N. C.
Blair, Augustine W., Guilford College, N. C.
Chamot, Emile M., Cornell Univ., Ithaca, N. Y.
Davis, Dr. Floyd, Des Moines, Iowa.
Haller, H. Loft, F.C.S., 27 Hilda St., Beverly Road, Hull, England.
Hotopp, C. H., Stroudsburg, Pa.
Kruskal, Dr. Nicholas, 72 Delancy St., N. Y. City.
Marlatt, Miss Abby L., Providence, R. I.
Meade, Richard K., Longdale, Alleghany Co., Va.
Patrick, George E., Dept. of Agr., Washington, D. C.
Slosson, E. E., Laramie, Wyo.
Smith, Prof. E. G., Beloit College, Beloit, Wis.
Stahl, Dr. Karl F., 57th St. and A. V. R. R., Pittsburg, Pa.
Tolman, Frank L., U. S. Naval Lab., Brooklyn, N. Y.

ASSOCIATE ELECTED SEPTEMBER 21, 1896.

Brinton, C. S., West Chester, Pa.

CHANGES OF ADDRESS.

Bachman, Irving A., Allentown, Pa.
Behr, Arno, 17 Lawn Ridge, Orange, N. J.
Doerflinger, Wm. F., 85 Lafayette Ave., Brooklyn, N. Y.
Boot, J. C., Brooklyn Distilling Co., Kent Ave., Brooklyn, N. Y.
Dal Molin, A. A., 30 E. 18th St., N. Y. City.
Davidson, Geo. H., 28 Woodbine St., Brooklyn, N. Y.
Fuller, Fred. D., Agr. Expt. Sta., Geneva, N. Y.
Habirshaw, William M., Glenwood Works, Yonkers, N. Y.

Hollick, Herbert, Post Office, New York City.
Kutroff, Adolph, 128 Duane St., New York City.
Loeb, Morris, 118 W. 72nd St., New York City.
Munsell, C. E., 110 Horatio St., New York City.
Sargent, Geo. W., Univ. of Pa., Dormitories, 37th and Spruce Sts., Philadelphia, Pa.
Thompson, F., 11 Willmot St., Ann Arbor, Mich.
Tidball, Walton C., 291 Prospect Pl., Brooklyn, N. Y.
Volckening, G. J., 65 Van Buren St., Brooklyn, N. Y.

MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

The first meeting for the year 1896–97 was held at Providence, on Thursday evening, September 24th, Chairman E. D. Pearce presiding.

Prof. J. H. Appleton read a paper upon the "Electrolysis of Salt."

The introduction to this paper was a brief discussion of the present chemical application of electricity. First in importance at present is the preparation of metals, copper, gold from cyanide solutions, zinc, glucinum, and even some more difficultly reducible metals or non-metals; sodium, lithium, cadmium, cobalt, nickel, and phosphorus. Next, reference was made to the production of certain compounds in which primarily the heat of the current is involved: silicon carbide, calcium carbide, as well as those metallic carbides, produced by Moissan, which, with water, yield such varied hydrocarbons (very suggestive in relation to the origin of petroleum).

The electrolysis of salt by several methods, notably Castner's, was next taken up.

In conclusion, there were presented some comments on the probable influence of the electrolysis of salt on the alkali industry.

NEW YORK SECTION.—ANNUAL MEETING.

OCTOBER 9, 1896.

The meeting was called to order at 8.20 P. M., by Dr. P. T. Austen, Chairman.

In the absence of the secretary, Dr. A. C. Hale was appointed secretary *pro tem.*

The minutes of the meeting held June 8th, 1896, were read and approved.

Reports of officers and committees being in order, the chairman called upon Dr. Hale to report for the delegates to the Scientific Alliance of New York. Dr. Hale made a brief oral report, which was accepted.

Dr. P. T. Austen, the retiring chairman of the section, reported on the work of the year and the general condition and prospects of the section and the society as well as the outlook for American chemists generally.

After these remarks by the retiring chairman the election of officers of the section for the ensuing year was held.

Dr. Durand Woodman was unanimously elected secretary and treasurer. Other officers were elected unanimously, as follows:

Chairman—Dr. Wm. McMurtrie.

Executive Committee—Dr. Charles A. Doremus, Prof. A. A. Breneman, Dr. Albert C. Hale.

Delegates to the Scientific Alliance of New York—Dr. Wm. McMurtrie, Dr. C. F. McKenna, Dr. C. A. Doremus.

Dr. Wm. McMurtrie, chairman-elect, then took the chair, and upon motion of Dr. Doremus, a vote of thanks to the retiring chairman was passed unanimously.

Prof. Breneman reported very encouraging progress in reference to the proposed chemical club.

Papers were read and discussed as follows: "Some Disputed Points about the Light of Carbon," by Woodbridge H. Birchmore; discussed by Prof. Speyers, Mr. Birchmore, and Mr. Stillwell. "The Conversion of Cow Milk into a Substitute for Human Milk," by Henry A. Bunker; discussed by Dr. Eccles, Dr. Bunker, and Dr. McMurtrie.

Upon motion of Dr. Doremus, seconded by Dr. Squibb, the following named persons were appointed a committee to cooperate with other scientific bodies in New York for the purpose of securing a lecture from Prof. Henri Moissan before his return to

France: C. A. Doremus, A. A. Breneman, M. Loeb, and Wm. McMurtrie.

Upon motion of Dr. Hale, the chairman of the section was authorized and requested to appoint a committee, with himself as chairman, to arrange the programs for the meetings of the section during the year.

The meeting then adjourned.

Issued with December Number, 1896.

Proceedings.

COUNCIL.

At the Buffalo meeting of the American Chemical Society it was voted that the Council be requested to take into consideration ways and means for bringing the Summer meeting of the Society into closer relation with that of Section C of the A. A. A. S., so that both meetings, if possible, may be held within the same week, thus affording the opportunity for all chemists to attend both meetings.

Inasmuch as both these bodies were well represented at the meeting referred to, it was suggested that a good deal of time could be gained by appointing then and there a committee of conference from each. This was accordingly done, the committee on the part of the American Chemical Society being Messrs. W. P. Mason, W. McMurtrie, Edward Hart, T. H. Norton and A. B. Prescott.

A joint meeting of this Committee was held with a Committee of Section C, and the following recommendations were agreed upon:

1st. Section C to have a business meeting for purposes of organization on Monday of the week of meeting, and the Vice-President's address to take place late in the afternoon of that day.

2nd. The American Chemical Society to be given Monday and Tuesday for their work.

3rd. Section C of the A. A. A. S. to be given the balance of the week.

4th. The arrangement of the program for the reading of papers before the two bodies to be left to the discretion of the President of the American Chemical Society and the Vice-President of Section C of the A. A. A. S.

These recommendations were approved by Council Oct. 27, 1896.

In view of the increasing number of papers presented at the meetings, the Council has decided that the Troy meeting shall extend over three days if this shall be found necessary.

NEW MEMBERS ELECTED NOVEMBER 5, 1896.

Andrews, Prof. W. W., Sackville, New Brunswick.
Burner, Prof. N. L., Ohio Med. Univ., Columbus, Ohio.
Case, Wm. A., Mt. Washington, Baltimore Co., Md.
Clark, Arthur W., Conshohocken, Pa.
Evans, Wm. Lloyd, Ohio State Univ., Columbus, O.
Fossler, Miss Mary L., 734 N. 9th St., Lincoln, Nebr.
Hochstetter, Robert W., Oak St. and Bellevue Ave., Cincinnati, O.
Levi, Louis E., Ph.D., 548 Franklin St., Buffalo, N. Y.
Mathews, John Alex., Columbia Univ., N. Y. City.
Mooers, Chas. A., Agr. Exp. Sta., Knoxville, Tenn.
Schoen, Joseph, 2317 Indiana Ave., Chicago, Ill.
Schroeder, J. Henry, Grand and Nassau Sts., Cincinnati, O.
Sturcke, H. E., 284 Pearl St., N. Y. City.
Sy, Albert P., Univ. of Buffalo, 24 High St., Buffalo, N. Y.
Wessling, Prof. Hannah L., 147 Milton St., Cincinnati, O.

ASSOCIATES ELECTED NOVEMBER 5, 1896.

Cooley, Fred. C., 1029 L St., Lincoln, Nebr.
Culver, Frank S., 1610 K St., Lincoln, Nebr.
Dales, Benton, 1242 P St., Lincoln, Nebr.
Himrod, George, 1446 Q St., Lincoln, Nebr.
Hiltner, Martin E., 1301 N St., Lincoln, Nebr.
Lange, Miss Helen P., 346 N. 17th St., Lincoln, Nebr.
O'Sullivan, Miss Eva, 445 N. 13th St., Lincoln, Nebr.
Pharmelee, Howard C., care of Cooperative Book Co., Lincoln, Nebr.
Thatcher, Roscoe W., 540 N. 15th St., Lincoln Nebr.

CHANGES OF ADDRESS.

Allen, Walter S., 34 So. 6th St., New Bedford, Mass.
Cushman, Allerton S., Chemical Laboratory, Harvard Univ., Cambridge, Mass.
Hancock, David, 1720 Fifth Ave., Birmingham, Ala.
Reese, Chas. L., 1801 Linden Ave., Baltimore, Md.
Sturm, Arthur B., Box 92, Maywood, Ill.

ADDRESS WANTED.

Bradley, Edson, formerly of 35 Broadway, New York City.

MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

A meeting of the Rhode Island Section was held at Providence, on Thursday evening, October 29, 1896.

Mr. E. D. Pearce mentioned the results of his experiments in bleaching brown tower acid. Samples of acid taken before and after bleaching were exhibited. Mr. Pearce also stated that the coloring matter of the anthers of the wild evening primrose was altered by acids and alkalies in the same way as turmeric.

A paper was read by W. M. Saunders upon "The Determination of Sulphur in Iron." The reader described briefly the deleterious effect of sulphur in iron. The small amount permitted in foundry work, and the difficulty of determining this amount was mentioned.

Next a description of methods of analysis was given. The reader considered the evolution methods, although not in every case giving the full sulphur contents of the iron, to be accurate enough for practical purposes. The results compare favorably with the oxidation method.

NEW YORK SECTION.

The November meeting of the New York Section was held on the 6th, Professor McMurtrie in the chair, and fifty-one members present.

The chair announced the acceptance by the executive committee of an invitation from Drs. Morton and Leeds to hold the December meeting at the Stevens Institute of Technology.

The death of Mr. Alfred H. Mason was announced and a sketch of his life was read.

A motion was made and seconded that the executive committee be recommended to authorize the secretary to employ a stenographer to report the discussions of papers presented at the meetings; such report, when properly edited, to be sent to the committee on papers, for publication in the Journal.

The following papers were read:

"The Volumetric Determination of Acetone," by Dr. E. R. Squibb.

"Notes on a Chemist's Trip Abroad," by C. A. Doremus.

"A New Form of Pyknometer," by J. C. Boot.

"Improvements in the Colorimetric Tests for Copper," by Geo. L. Heath.

"Note on Solubility of Bismuth Sulphide in Alkaline Sulphides," by Geo. C. Stone.

The meeting then adjourned.

CINCINNATI SECTION.

The meeting was held on November 17, in the Lloyd Library. After welcoming the Society, Prof. J. U. Lloyd read a paper entitled "Bibliography of American Pharmacy," giving a concise history of the different editions of the U. S. Pharmacopeia and its commentaries, the various dispensatories and formularies. This paper was rendered doubly interesting by the exhibition of the rare old editions of these works from the well-filled shelves of the Lloyd Library. Prof. O. W. Martin read a paper opening the discussion on the "Teaching of Elementary Chemistry." A contribution on this subject by Dr. James Lewis Howe was read by Mr. H. B. Foote. Excerpts from paper which Prof. Paul Freer presented at the summer meeting of American Association for the Advancement of Science, elicited considerable discussion by Dr. Springer, Profs. Norton, Martin and Homburg.

Dr. William H. Crane, of Cincinnati was elected a member of the Section.